Asymmetric catalysis using novel platinum complexes

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Asymmetric Catalysis using Novel Platinum Complexes

by

Matthew Lee Clarke

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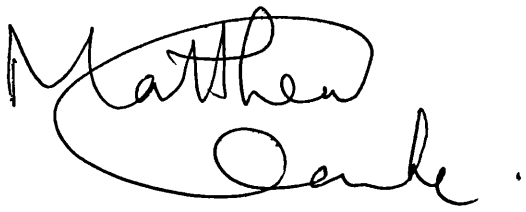

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Abstract

This thesis discusses, as the title suggests, the synthesis and characterisation of new platinum complexes, and their evaluation as catalysts for several organic processes.

The first chapter acts as an introduction by describing some existing reactions that are catalysed by platinum complexes.

The second chapter concerns itself with the co-ordination chemistry of the enantiomerically pure, P,N bidentate ligand which was used throughout my studies. The preparation of novel cationic platinum complexes that behave as Lewis acids is also described, as is there application as efficient catalysts for three different carbon-carbon bond forming reactions.

The development of a highly enantioselective platinum catalysed allylic alkylation reaction is described in some detail in chapter three. The studies have revealed interesting differences between platinum and palladium catalysts, which give information on the different characteristics of the two metals in general.

In chapter four, the regioselectivity of nucleophilic attack in platinum catalysed allylic alkylation is fully addressed. These studies revealed an unexpected, and intriguing ligand effect that operates with both palladium and platinum catalysts. This ligand effect was studied with respect to both its origin and its synthetic utility.

Acknowledgements

I would like to take this opportunity to thank the many people from the chemistry (and other) departments at the University of Bath who have helped me out during my PhD.

Particular mention goes to the following people who I am indebted to, in varying proportions, for their friendship, technical assistance, good idea's, and good humour.

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I would like to thank my parents and my brother, for being just about ideal in most respects.

Finally, I would like to thank my beloved girlfriend, Jane, for playing the key part in the good times I have had over the last three years. She also deserves thanks for proof-reading thisk thesizk.

Contents

Abbreviations

Ac	acetate
Ar	aryl
app.	apparent
aq.	aqueous
BINOL	1,1'binaphthol
bipy	bipyridine
br	broad
BSA	N,O-bis(trimethylsilyl)acetamide
C. I.	Chemical Ionisation
Cy	cyclohexyl
COD	1,5-cyclo-octadiene
d	doublet
dba	dibenzylideneacetone
DCM	dichloromethane
dd	doublet of doublets
ddd	doublets of doublets of doublets
d.e.	diastereomeric excess
decomp	decomposition
DIOP	2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
DIPT	diisopropyl tartrate
dm	double of multiplets
DMAD	dimethyl acetylenedicarboxylate
DMAP	4-dimetylaminopyridine
DME	dimethoxyethane
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dq	doublet of quartets
dt	doublet of triplets
e.e.	enantiomeric excess

Et	ethyl
F. A. B	Fast Atom Bombardment
F. T. I. R	Fourier Transform Infra Red
G. C.	Gas Chromatography
hept.	heptet
hex	hextet
H. P. L. C.	High Performance Liquid Chromatography
Hz	Hertz
I. R.	Infra Red
m	multiplet
m-CPBA	*meta*-chloroperbenzoic acid
Me	methyl
NMO	*N*-methyl morpholine-*N*-oxide
NMR	Nuclear Magnetic Resonance
Oct	octyl
ppte	precipitate
Pr	propyl
q	quartet
qn	quintet
req.	require
s	singlet
t	triplet
Tf	triflate
T. L. C.	Thin Layer Chromatography
THF	tetrahydofuran
TMEDA	*N,N,N,N'*-tetramethylethylenediamine
TMS	tetramethylsilane
tm	triplet of multiplets
U. V.	Ultra Violet

Chapter 1

Homogeneous Catalysis using Platinum Complexes.

The thesis you are about to read has a theme running throughout it: New platinum complexes have been prepared, and shown to catalyse a variety of organic reactions. As an introduction to this, it seems logical to discuss the organic chemistry that can be mediated by platinum complexes. Due to the limitations of space, this discussion will focus on homogeneous catalysis and in particular, highlight examples where the use of platinum enables a process that is not possible with other metal catalysts.

However, first of all it is important to mention the contribution that the study of platinum complexes has made in elucidating the mechanism of several transition metal catalysed reactions. Platinum complexes have two key advantages as tools to understanding mechanisms: ^{195}Pt is an NMR active isotope, and consequently NMR is a particularly useful tool for characterisation. Pt-L coupling constants give information on the nature of the bonding in a given complex. Secondly, many compounds which are transient intermediates for other metals can often be isolated and fully characterised for similar platinum complexes. The organic chemistry of platinum goes right back to 1830 when the first organometallic compound, "Zeise's salt", $K[Pt(C_2H_4)Cl_3] . H_2O$ was prepared.[1] Since that time the reactivity of a large number of platinum-olefin complexes has been outlined, and these studies can be regarded as the direct ancestors of the many transition metal catalysed processes that involve metal-olefin complexes. More recently, platinum complexes that resemble possible intermediates in a catalytic cycle have been used to help deduce the mechanism of a number of important reactions (particularly nickel and palladium catalysed processes).

It is worth noting at this stage some general properties of platinum complexes, and in particular, how platinum compares to palladium, which is probably the most commonly employed metal in organic synthesis. Platinum has three main oxidation states, 0, II, and IV, and it is straightforward to go between them by oxidative addition and reductive elimination processes. Platinum is classified as one of the softest metals, and resultantly forms stronger bonds with soft ligands. The zerovalent platinum complexes are frequently more stable (to air, water and electrophiles) than related palladium complexes and often require more forcing conditions for oxidative addition of an organic substrate to occur. For instance, aryl bromides and iodides readily oxidatively add to palladium complexes at 65 °C and below, whereas otherwise identical platinum complexes only undergo the reactions at about 100 °C.

Both Pt^{0} and Pt^{II} alkene and alkyne complexes are thought to be somewhat more stable than their palladium analogues. Backbonding from platinum to the unsaturated compound is thought to be more significant for platinum complexes. Palladium activates alkenes more strongly to nucleophilic attack.
Platinum(IV) complexes have been reported more often in the literature than palladium(IV) complexes, and the redox cycle Pt^{II}- Pt^{IV}- Pt^{II} has been more fully documented.
Platinum σ-alkyl and σ-aryl complexes are more stable (to decomposition) than those of palladium (which are much more stable than nickel complexes). The decomposition pathway for bis-alkyl and aryl complexes is generally reductive

elimination with coupling of the two organic ligands. This is the basis of nickel and palladium catalysed cross coupling reactions. The related organoplatinum complexes, however, are stable up to quite high temperatures.

Divalent platinum binds strongly to nitriles, imines, and sulphur containing compounds. These compounds donate electrons to the platinum centre, which suggests that platinum complexes may be of use as Lewis acid catalysts. Whereas platinum has amongst the strongest affinity for sulphur ligands (soft metal- soft ligand), oxygen ligands generally form fairly labile complexes (more labile than palladium or nickel). The remainder of this chapter discusses how some of the properties of platinum complexes have been applied to homogeneous catalysis.

1: Hydrosilylation

Platinum complexes are excellent homogeneous catalysts for hydrosilylation of olefins, dienes, and alkynes and are used in commercial processes. Many of the early studies focused on the use of H_2PtCl_6 as catalyst.[2] The reactivity and selectivity of the process is highly dependent on the olefin and silane used, and in some instances the catalysis is probably heterogeneous. In some cases isomerisation occurs during catalysis. For example, internal olefins can give primary silane products (Fig.1.1).[2]

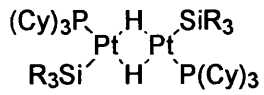
$$Cl_2CH_3SiH + CH_3CH{=}CH_2CH_3 \xrightarrow{\text{cat. } H_2PtCl_6} CH_3(CH_3)CH_2Si(CH_3)Cl_2$$

Fig. 1.1

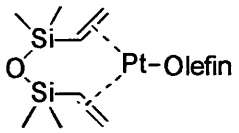
In the case of terminal alkenes which do not tend to isomerise, the silicon atom generally adds to the least substituted carbon atom of the double bond, and the Pt catalysts are therefore not especially suitable as asymmetric catalysts.[3]

A more active catalyst than H_2PtCl_6 alone is known as the Karstedt catalyst.[4] This catalyst is the product of reaction of H_2PtCl_6 and $(CH_2{=}CHSiMe_2)_2O$.

It as thought that the zerovalent platinum complex $[Pt_2(CH_2{=}CHSiMe_2)_2O)_3]$ is the actual catalyst. Stone and co-workers prepared complex **(1)**, a catalyst for hydrosilylation that gives products with less isomerisation and can be used at room temperature.[5]



(1)



(2)

Fig. 1.2

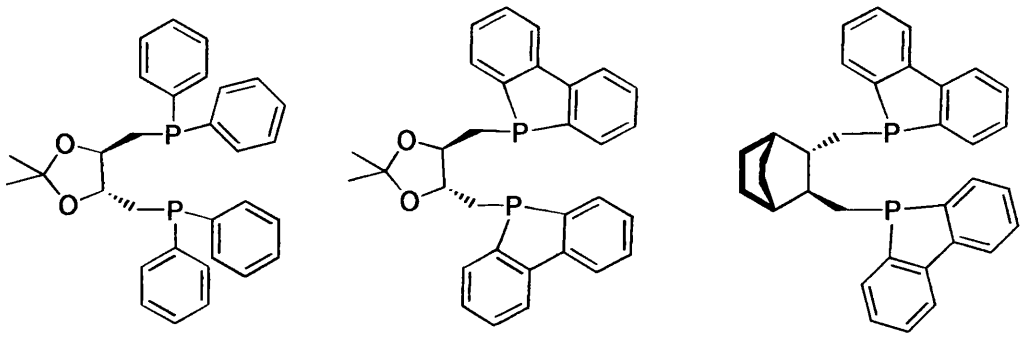
This complex is also used in hydrosilylation of alkynes and catalyses the reaction without heating after briefly warming the reactants. Previous catalysts required temperatures up to 150 °C to yield the desired product.[6] Recently, Steffanut, Osborn, DeCian and Fischer have rationally designed even more active catalysts, **(2)**, by adding electron poor olefins to the Karstedt catalyst.[7]

Platinum also catalyses the related process hydrogermination of alkenes (addition of R_3Ge-H to a C=C bond).[8]

2: Hydroformylation

In terms of activity, platinum complexes also make very good hydroformylation catalysts.[9, 10] The complexes of choice are generally a mixture of a bis-phosphine dichloride complex, $(R_3P)_2PtCl_2$ and $SnCl_2$ co-catalyst. The reaction conditions have to be carefully controlled as hydroformylation can be accompanied by

isomerisation and hydrogenation. The regioselectivity is generally in favour of linear products, and they are therefore not always the catalysts of choice for asymmetric hydroformylation. (DIOP)$PtCl_2$ / $SnCl_2$ systems generally give moderate (10-50%) e.e.. It has been found that if the diphenylphosphino groups of DIOP **(3)** are exchanged for a dibenzophosphole (BDP) group as in ligand **(4)**, the regioselectivity is reversed and predominantly branched, chiral products are formed (Fig. 1.4). Ligand **(5)**, which is also modified by dibenzophosphole groups, gives better selectivity than its diphenylphosphino- analogue.[9, 10, 11]



(3) **(4)** **(5)**

Fig. 1.3

(6) **(7)** **(8)** **(9)**

using DIOP, **(3)** as ligand: **(7) : (8) : (9)** = 21 : 69 : 10

using BDP-DIOP, **(4)** as ligand: **(7) : (8) : (9)** = 62 : 18 : 20

Fig. 1.4

3: Hydrogenation

The same types of platinum complexes that catalyse hydroformylation make good hydrogenation catalysts. Probably the most synthetically useful study showed that polyunsaturated esters (such as those in soya bean oil) could be selectively hydrogenated to monounsaturated esters.[13] The degree of hydrogenation and isomerisation was dependent on the olefin starting material

4: Carbonylation and related processes

A mix of H_2PtCl_6 and $SnCl_2$ catalyses carbonylation of terminal alkenes to afford predominantly linear methyl esters (if MeOH is present) or acids (if H_2O is present) with good yields and under relatively mild conditions (Fig. 1.5).[14]

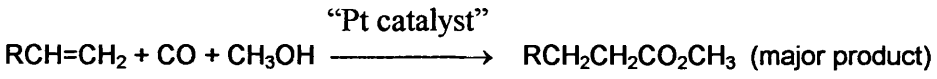


Fig. 1.5

A related reaction reported very recently is the [4+1] cycloaddition of vinyl allenes with carbon monoxide which is catalysed efficiently by $Pt(COD)_2$ (Fig. 1.6). A rhodium complex also catalyses this reaction equally effectively.[15]

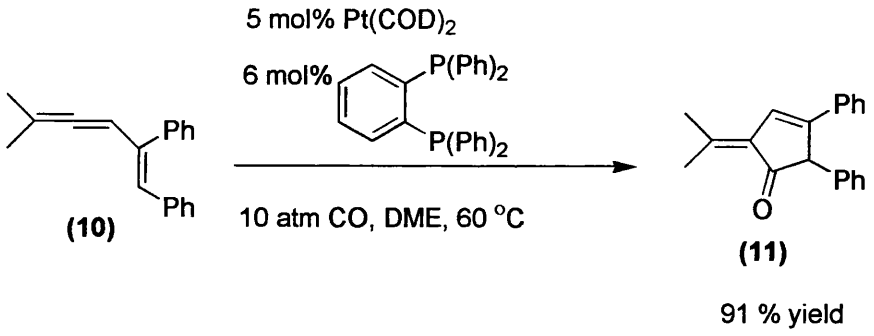
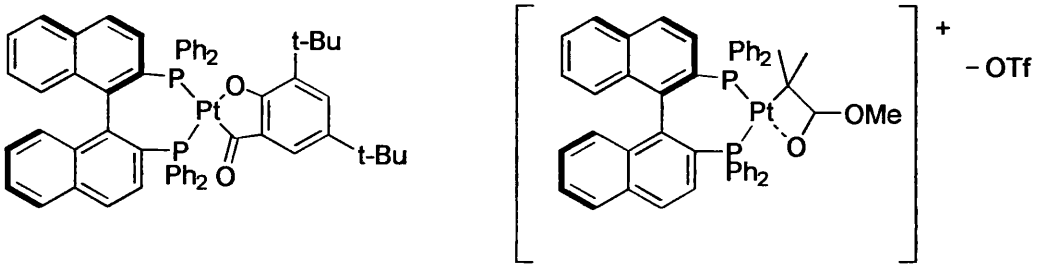


Fig. 1.6

Another reaction which takes place under carbon monoxide pressure is the reduction of nitroarenes to aminoarenes.[16] This reaction is both high yielding and chemoselective.

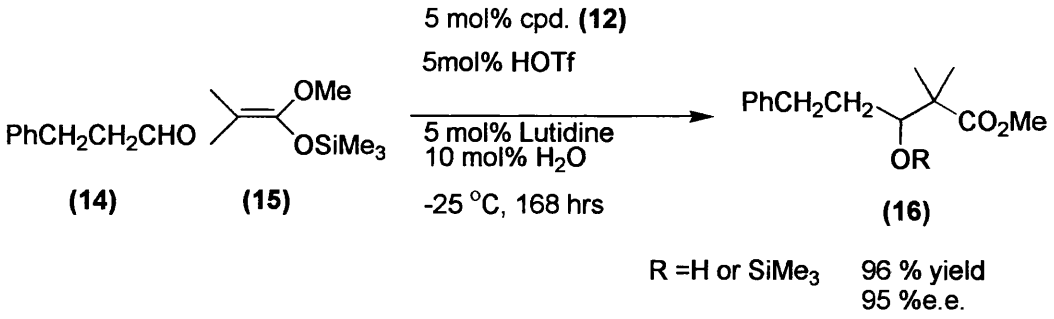
5: Aldol reactions

Platinum complexes such as **(12)** can be activated with triflic acid to generate catalysts for the aldol reaction of ketene silyl acetals with aldehydes (Fig. 1.8).[17] Air, water and a proton scavenger must be present during the catalyst activation stage in order to give an enantioselective catalyst (products which were racemic in the absence of the above additives had 95 % e.e. under optimised conditions). The reaction, which is rather slow, is thought to proceed through the enolate complex such as **(13)**.



(12) **(13)**

Fig. 1.7



(14) **(15)** **(16)**

Fig. 1.8

Togni and co-workers have prepared complex **(17)** and shown it to be a good catalyst for the aldol reaction of isocyanoacetates (Fig. 1.9). [18]

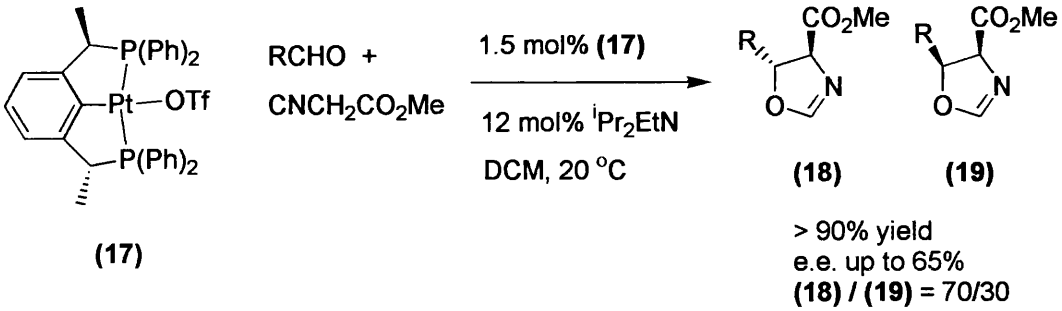


Fig. 1.9

Gold complexes of ferrocenyl phosphines that contain an internal base make far superior catalysts however, and constitute one of the most ingenious catalytic processes designed to date. [19]

Another reaction which involves metal enolates is the $(Et_3P)_3Pt$ catalysed deuteration of carbonyl compounds (Fig. 1.10). [20]

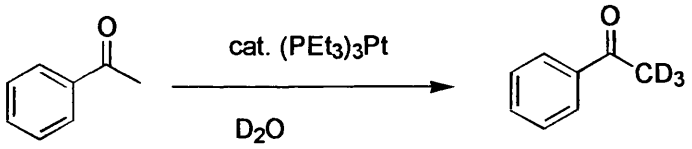


Fig. 1.10

6: Hydration reactions

$(Cy_3P)_2Pt$ is an efficient catalyst for hydration of nitriles.[20] More recently complex **(20)** has been shown to be an especially active catalyst for this type of reaction.[20(b)]

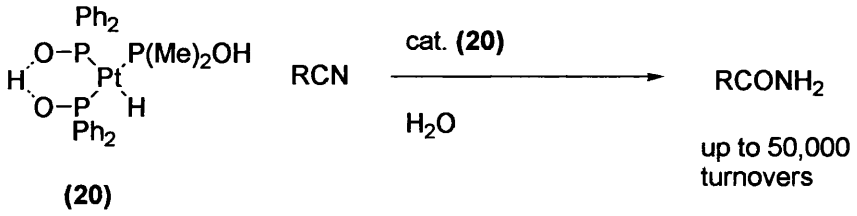


Fig. 1.11

The hydration of unactivated alkynes is a useful reaction and platinum is one of the catalysts of choice (Fig. 1.12). Both Zeise's dimer, $[PtCl_2(C_2H_4)]_2$ and $PtCl_2$ have been found to be more selective than mercury catalysts that were used industrially at that time.[21]

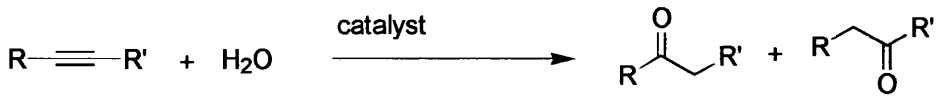
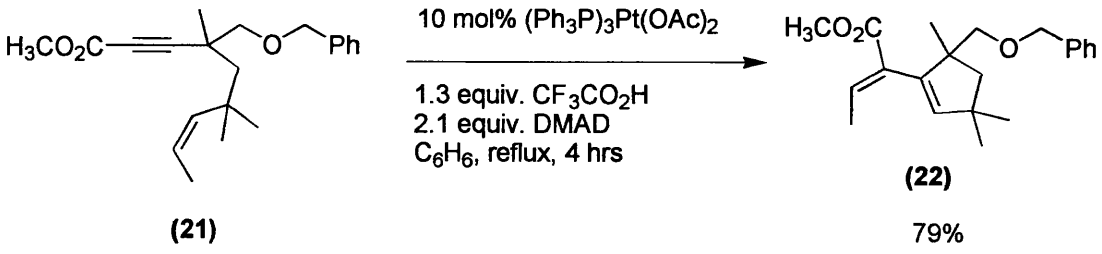


Fig. 1.12

$PtCl_4$ and CO has also been found to be a good catalytic system for this reaction.[22] A combination of (dppe)$PtCl_2$ and silver salts catalyses addition of methanol to non-activated internal alkynes.[23]

7: Enyne metathesis

Another way that platinum complexes can elaborate alkynes in organic synthesis was reported by Trost and co-workers in 1993. Enynes undergo a metathesis reaction to form vinyl substituted cycloalkenes (Fig. 1.13).[24] While most of this work focused on palladium catalysts, the use of $(Ph_3P)_2Pt(OAc)_2$ catalyst was at least as effective as comparable palladium systems. $PtCl_2$ has also been found to be a good catalyst for this reaction.[25]



(21) **(22)**

79%

Fig. 1.13

8: Reactions mediated by insertion into diazo compounds.

It has recently been found that platinum complexes are the best catalysts for the insertion of diazo compounds into O-H bonds of alcohols (Fig. 1.14). The reactions show high yield, catalytic turnover and chemoselectivity.[26]

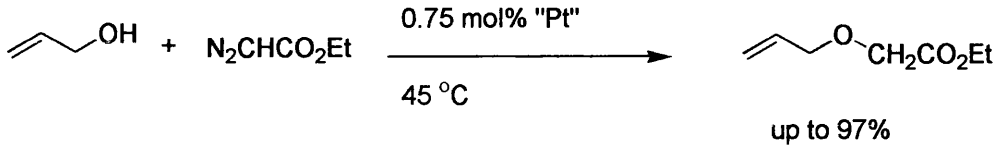


Fig. 1.14

Platinum complexes also catalyse the cyclopropanation of olefins. This important reaction can also be catalysed by a selection of other transition metal complexes.[27]

9: Ring cleavage reactions

Cyclopropanes themselves undergo platinum catalysed ring opening to give either olefins, ketones or ethers.[28] Platinum complexes appear to be the best catalysts for this reaction, which proceeds through a platinacyclobutane intermediate like complex **(24)**. In Fig.1.15, the result is a stereoselective addition of alcohol across the cyclopropane bond next to the ether functionality.

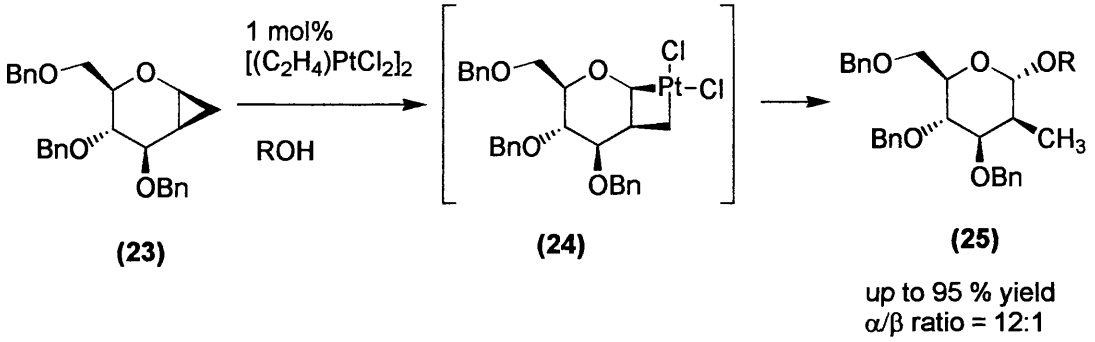
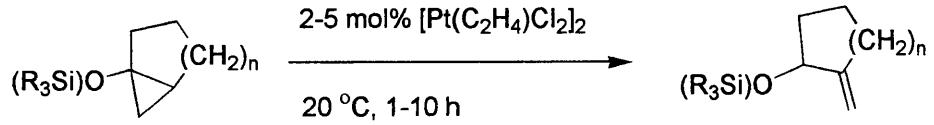


Fig. 1.15

Fig. 1.16 shows 2-5 mol% of Zeise's dimer catalysing isomerisation of siloxycyclopropanes to allyl silyl ethers. This reaction proceeds readily for a wide

range of siloxycyclopropanes and is also assumed to proceed through a platinacyclopropane.[28(b)] Alkoxy or hydroxy cyclopropanes isomerise to α-methyl ketones under similar conditions.[28(c)]



(26) **(27)**

Fig. 1.16

A reaction which is related to the above process is platinum promoted methylation of epoxides (Fig. 1.17).[29]

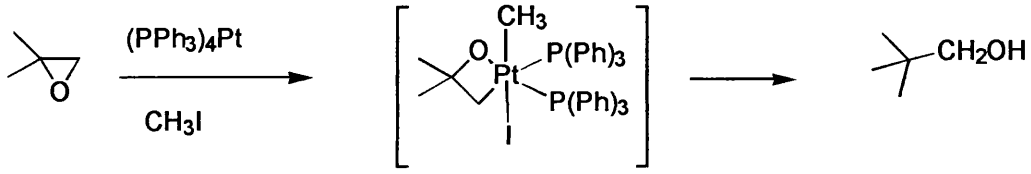


Fig. 1.17

10: Stille coupling

In the course of mechanistic studies on the Hiyama reaction (coupling of organosilanes with organic electrophiles), it has been shown that $(Ph_3P)_4Pt$ catalyses the Stille coupling reaction (Fig. 1.18). However, the reaction is slower compared to related palladium complexes.[30]

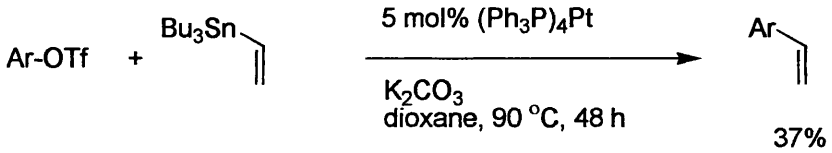


Fig. 1.18

11: Addition of stannanes and distannation

Platinum catalyses addition of aldehydes or imines with allyl stannanes (Fig. 1.19). Although palladium complexes also catalysed this reaction, $(Ph_3P)_2PtCl_2$ gave the highest yields.[31]

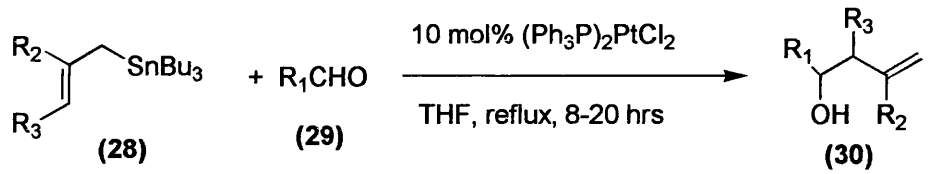


Fig. 1.19

$(Ph_3P)_2Pt$-ethylene catalyses the distannation of **(31)** to activated terminal alkynes to give the 1,4-distanna[4]ferrocenophanes (Fig. 1.20).[32]

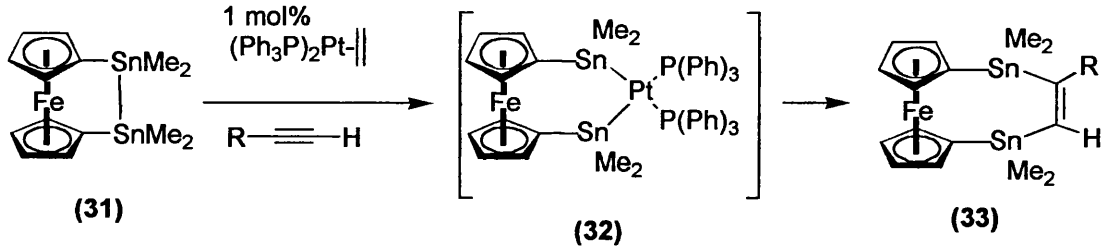


Fig. 1.20

12: bis-Silylation

$(Ph_3P)_2Pt$-ethylene can catalyse the related bis-silylation of unsaturated hydrocarbons but is a much less active catalyst than related Pd compounds.[33]

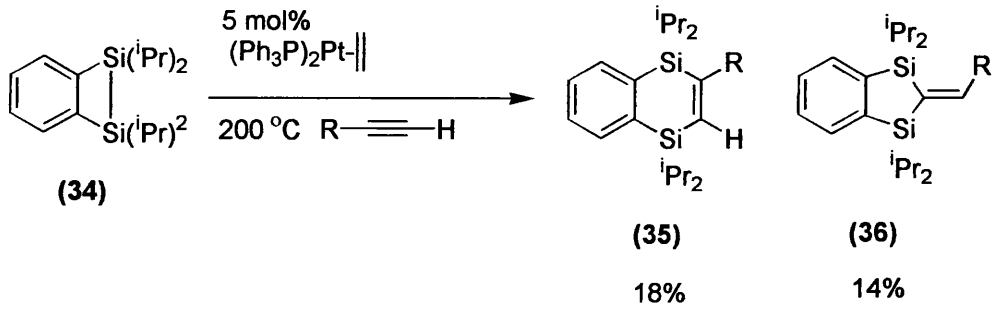


Fig. 1.21

13: Silaboration

The addition of Si-B bonds to a multiple bond (silaboration) is of some interest and is also catalysed by platinum complexes. $(Ph_3P)_4Pt$ is a good catalyst for silaboration of alkynes (Fig. 1.22) (but somewhat less active than palladium *tert*-alkylisocyanide complexes).[34]

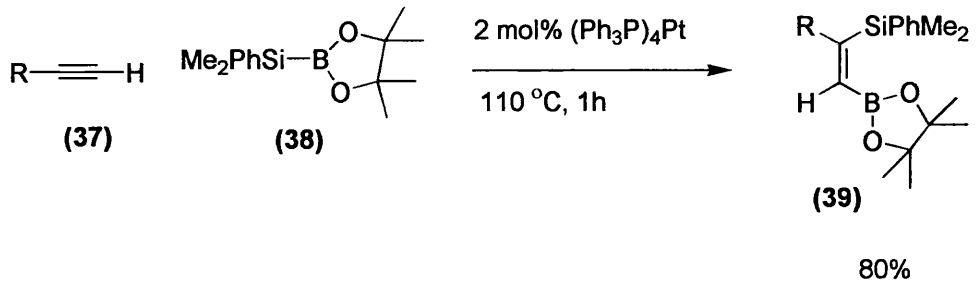


Fig. 1.22

Platinum complexes, however, are the best catalysts for silaboration of terminal alkenes. This reaction, which is not catalysed by the palladium *tert*-alkylisocyanide complex, shows the opposite regiochemistry to silaboration of alkynes (Fig. 1.23).[35]

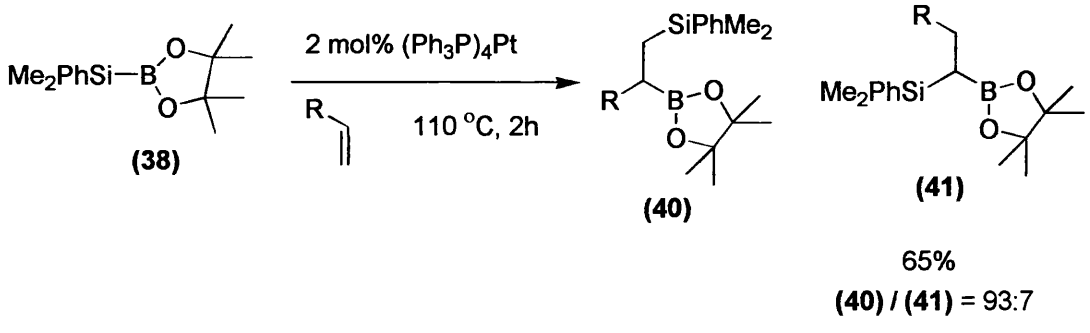


Fig. 1.23

Silaboration of 1,3 dienes, **(42)** proceeds by a 1,4 addition. The alkene, **(43)** is a 1:1 mixture of stereoisomers (Fig. 1.24).[36]

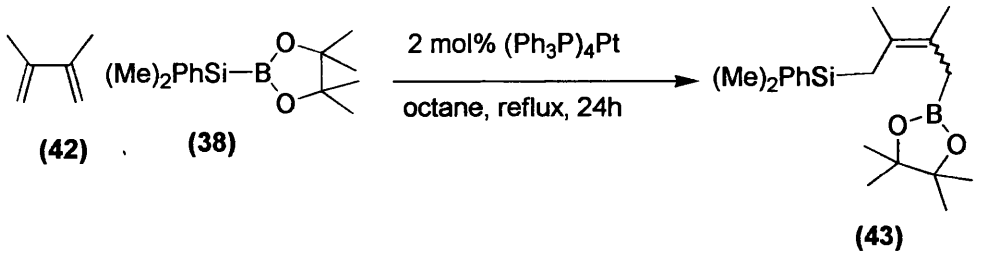


Fig. 1.24

If this same reaction is carried out in the presence of aldehydes, a change in reaction pathway is observed and **(45)** is formed (Fig. 1.25).

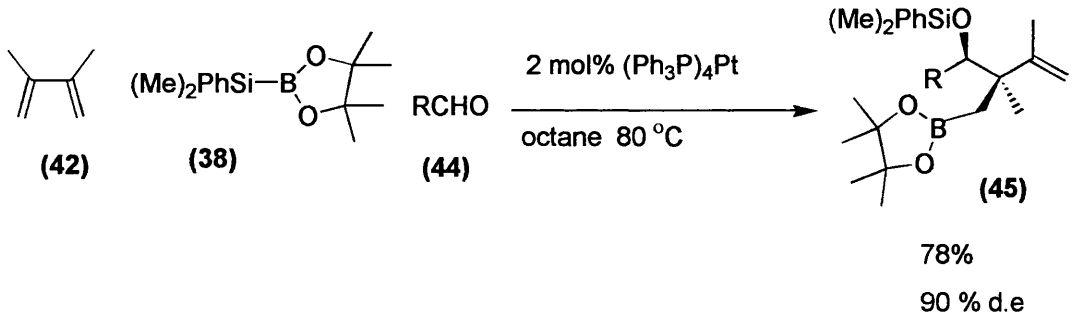


Fig. 1.25

14: Thiosilylation

A different approach for the introduction of two different heteroatoms to an unsaturated compound has been reported.[37] A variety of terminal alkynes undergo the thiosilylation reaction shown in Fig. 1.26 in the presence of $(Ph_3P)_2Pt$-ethylene catalyst to form **(49)**. It was proposed that $(ArS)_2$ and $(SiCl_3)_2$ undergo a Pt catalysed disproportionation to form $ArS\text{-}SiCl_3$ prior to the platinum catalysed addition to the triple bond.

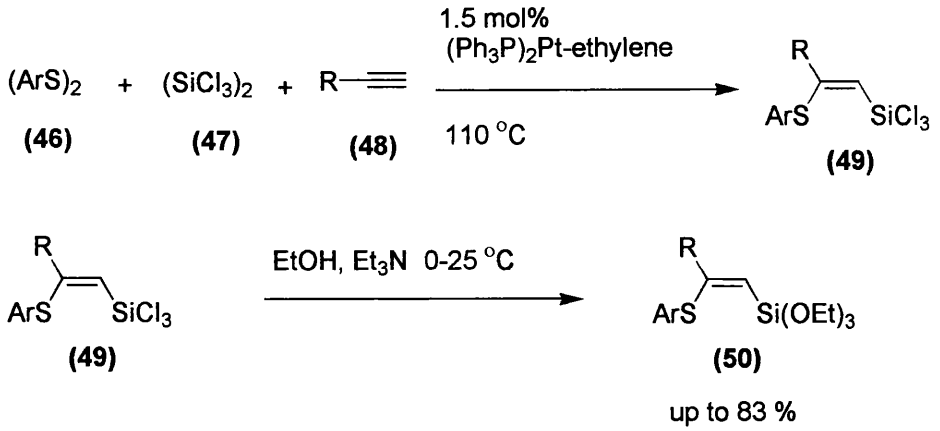


Fig. 1.26

15: Diboration

The diboration of unsaturated hydrocarbons has recently received much interest. Platinum complexes are the catalysts of choice for this reaction. $(Ph_3P)_4Pt$ or $(Ph_3P)_2Pt$-ethylene are good catalysts for addition of B-B bonds to alkynes and 1,3 dienes.[38] The likely mechanism is shown in Fig. 1.27.

For the related addition to olefins, these complexes are not successful. Having found evidence that the phosphine ligand and the unsaturated substrate compete for a co-ordination site,[39] phosphine free catalysts such as $(COD)_2Pt$ and $Ptdba_2$ were investigated. Three mol% of these compounds allows excellent yields of diboration product, **(53)** under mild conditions (Fig. 1.28).[40]

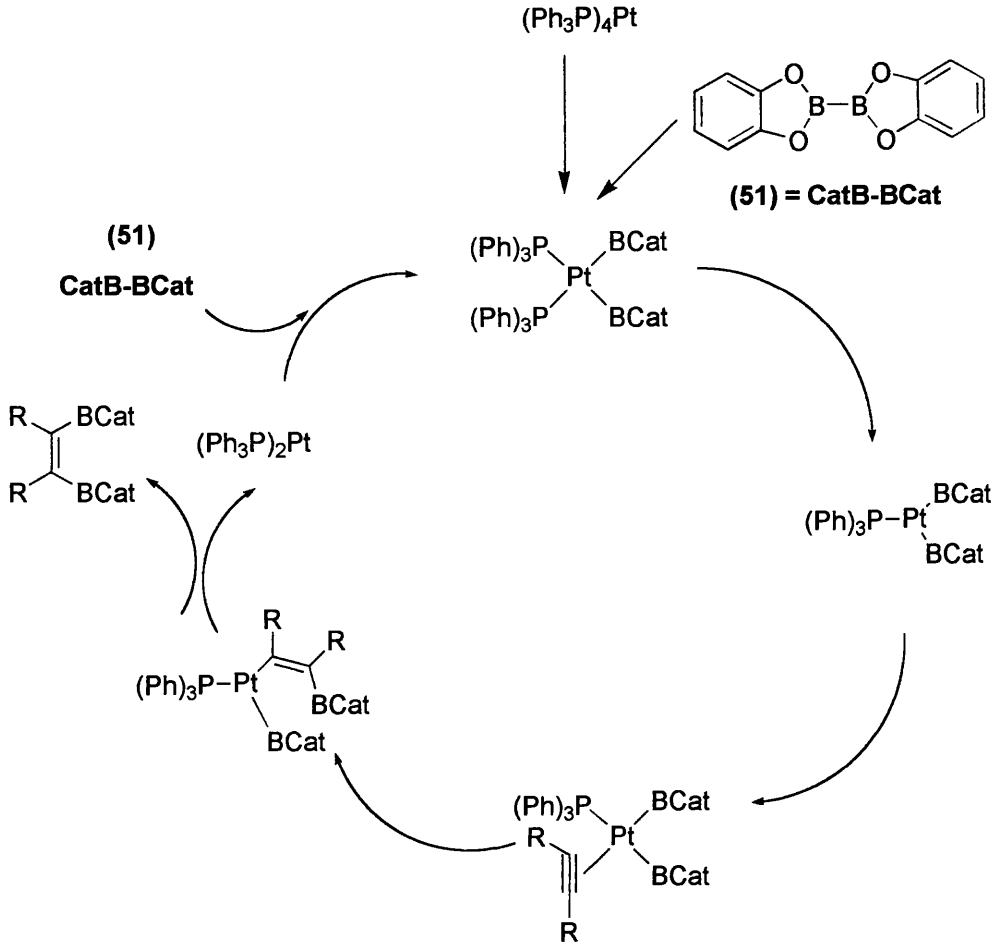


Fig. 1.27 Proposed catalytic cycle for platinum catalysed diboration of alkynes

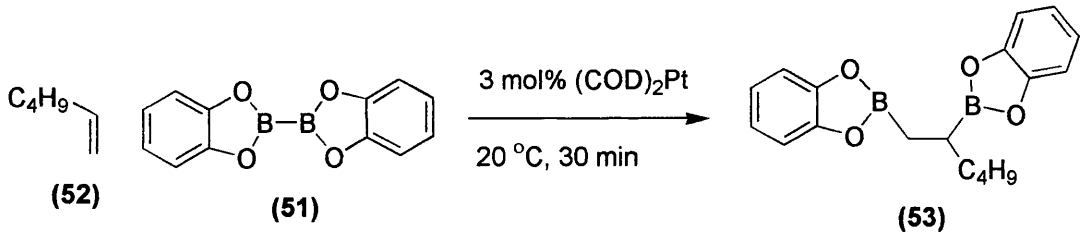


Fig. 1.28 Platinum catalysed diboration of olefins

An asymmetric diboration of alkenes using enantiopure diboranes derived from enantiopure diols has been developed and gives moderate d.e. [41]

Diboration of allenes such as substrate **(54)** is also possible using either $(Ph_3P)_4Pt$ or $Pt(dba)_2$ / phosphine (1:1). Interestingly, the use of tricyclohexylphosphine gave a much more active catalytic system and altered the regioselectivity (Fig. 1.29).[42]

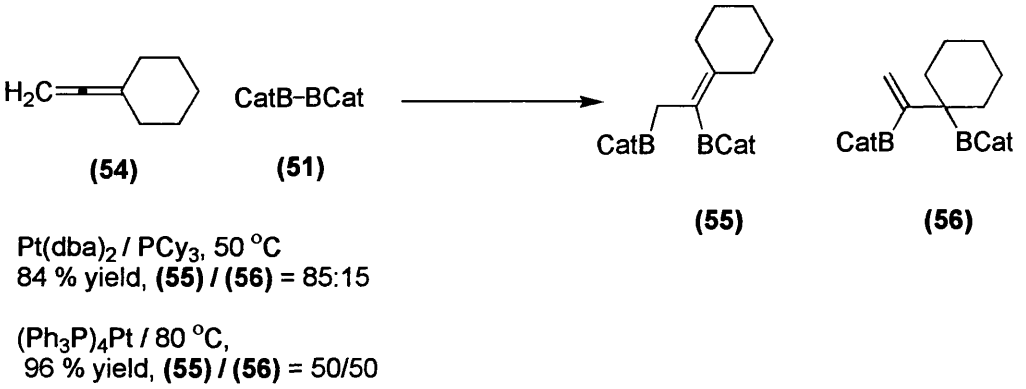


Fig. 1.29

16: Hydrophosphination

Platinum complexes are the most well studied catalysts for addition of P-H bonds to unsaturated substrates. K_2PtCl_4 catalyses addition of phosphine gas to formaldehyde to give the alkyl phosphine, $P(CH_2OH)_3$.[43]

Another example is 0.2 mol% of $[(EtO_2CCH_2CH_2)_3P]_3Pt$ catalysing formation of $(EtO_2CCH_2CH_2)_3P$, **(57)** from phosphine gas and ethylacrylate (Fig. 1.30).[44]

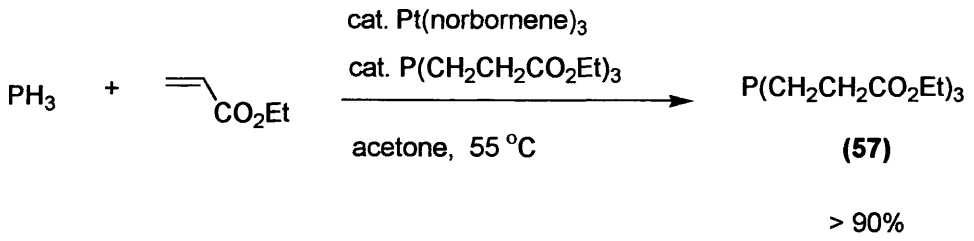


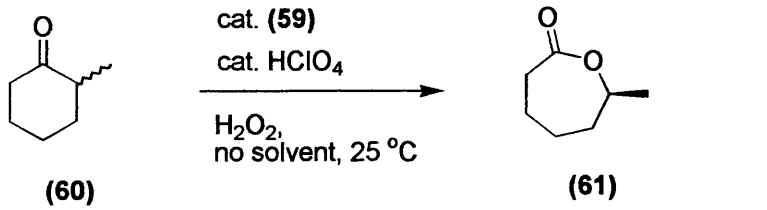
Fig. 1.30

Platinum complexes of type **(58)** catalyse Baeyer-Villiger oxidation using dilute hydrogen peroxide as oxidant.[45] The catalysts only deliver moderate conversions and are deactivated as conversion increases.

When complex **(59)** is used as catalyst, moderate e.e. and conversion in the oxidation of ketone **(60)** can be obtained (Fig. 1.32). It is necessary to activate the catalyst with $HClO_4$ prior to reaction.[46]

(58) **(59)**

Fig. 1.31



(60) **(61)**

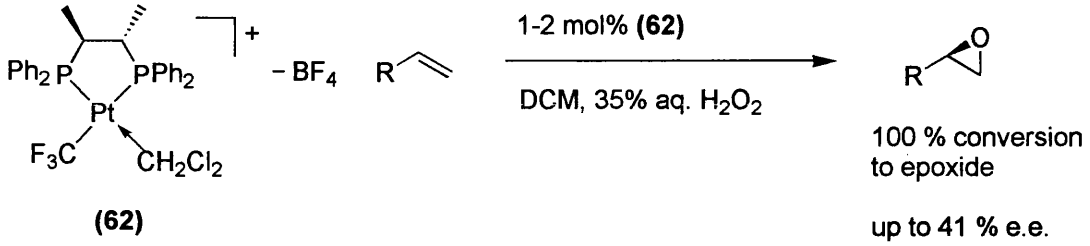
37 %e.e. at 30 % conversion

Fig. 1.32

Platinum diphosphine complexes containing a trifluoromethyl ligand like complex **(58)** are also able to catalyse the epoxidation of terminal alkenes with hydrogen peroxide.[47] The platinum complex performs a bifunctional role in aiding the formation of the hydroperoxide anion and by acting as a binding site for the alkene, rendering it more prone to nucleophilic attack.

This process was made enantioselective by using complex **(62)** derived from the chiral diphosphine ligand, chiraphos.[48] This catalyst achieved the highest e.e., at the time, for a metal catalysed epoxidation of a terminal alkene, (41 %) (Fig. 1.33).

It is this platinum catalysed reaction which first aroused our interest in platinum complexes as asymmetric catalysts, and our initial aim was to find complexes that might improve on the result described above.



(62)

Fig. 1.33

Chapter 2

Synthesis and Structure of Enantiomerically Pure Platinum Complexes of Phosphino-oxazolines and their use in Asymmetric Catalysis

2.1 Background:

The enantioselective epoxidation of alkenes is an important organic transformation. Epoxides are valuable building blocks in the synthesis of many molecules and there is a large demand for epoxides to be synthesised as one enantiomer. In fact, there have been major advances in this field in the last 20 years. The system developed by Sharpless *et. al.*[49] epoxidises allylic alcohols stereoselectively and has been converted into an industrial process. The ingredients used for a catalytic Sharpless epoxidation are titanium (IV) isopropoxide, diethyl tartrate (or other enantiopure tartrate esters) ^{t}butyl hydroperoxide and molecular sieves. Molecular sieves are crucial if the reaction is to be catalytic. A very thorough account on developing optimum reaction conditions has been published.[50] One of the simplest, but most useful examples is shown in Fig. 2.1. Allyl alcohol can be epoxidised to produce either enantiomer of (nearly) optically pure glycidol. Additionally, the glycidol, which can be difficult to isolate, can be derivatised *in situ*, and this has been used in the synthesis of several drugs and natural products.[50]

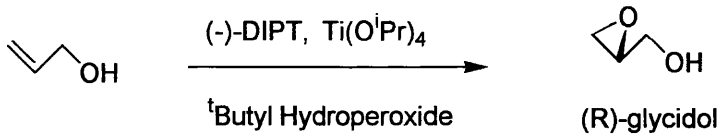
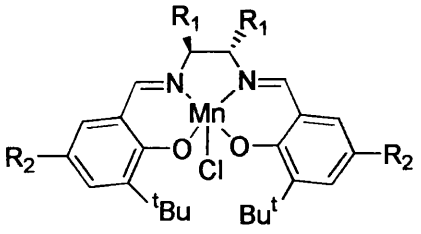


Fig. 2.1

The manganese (III) salen complexes developed by Jacobsen and Katsuki have the general structure shown overleaf. They are the best transition metal catalysts for enantioselective epoxidation of unfunctionalised cis alkenes.[51]



R_1 = Ph or -(C_4H_8)-

R_2 = Me, OSi(^{i}Pr)$_3$, OMe

Catalyst, **(63)**, R_1 = Ph, R_2 = OSi(^{i}Pr)$_3$

Fig. 2.2

The original procedure used bleach as oxidant and epoxidises a variety of cis unfunctionalised alkenes with good to excellent e.e.. The use of m-CPBA / N-methylmorpholine-N-oxide as oxidant increases reactivity and allows the epoxidation to be carried out at -78 °C. Excellent e.e.'s for cis alkenes can be obtained at this temperature, and epoxidation of some styrenes [52] now gives good enantiomeric excess. Epoxidation of trans alkenes with good e.e. can be carried out with modified chromium salen complexes.[53] However, there are still no effective methods for enantioselective epoxidation of terminal alkenes. A method for producing enatiomerically pure terminal epoxides by resolution of a racemic mixture has recently been described by Jacobsen and co-workers.[54]

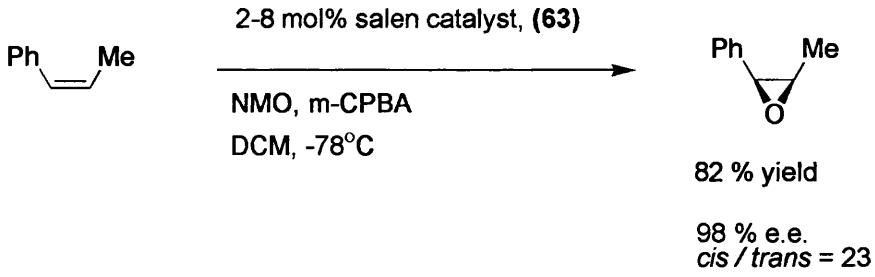


Fig. 2.3

We felt that the platinum catalysed reaction described by Strukul, Michelin and co-workers represented one of the most interesting attempts at filling this gap in methodology.[47, 48] The proposed mechanism of their process is shown in Fig. 2.4.

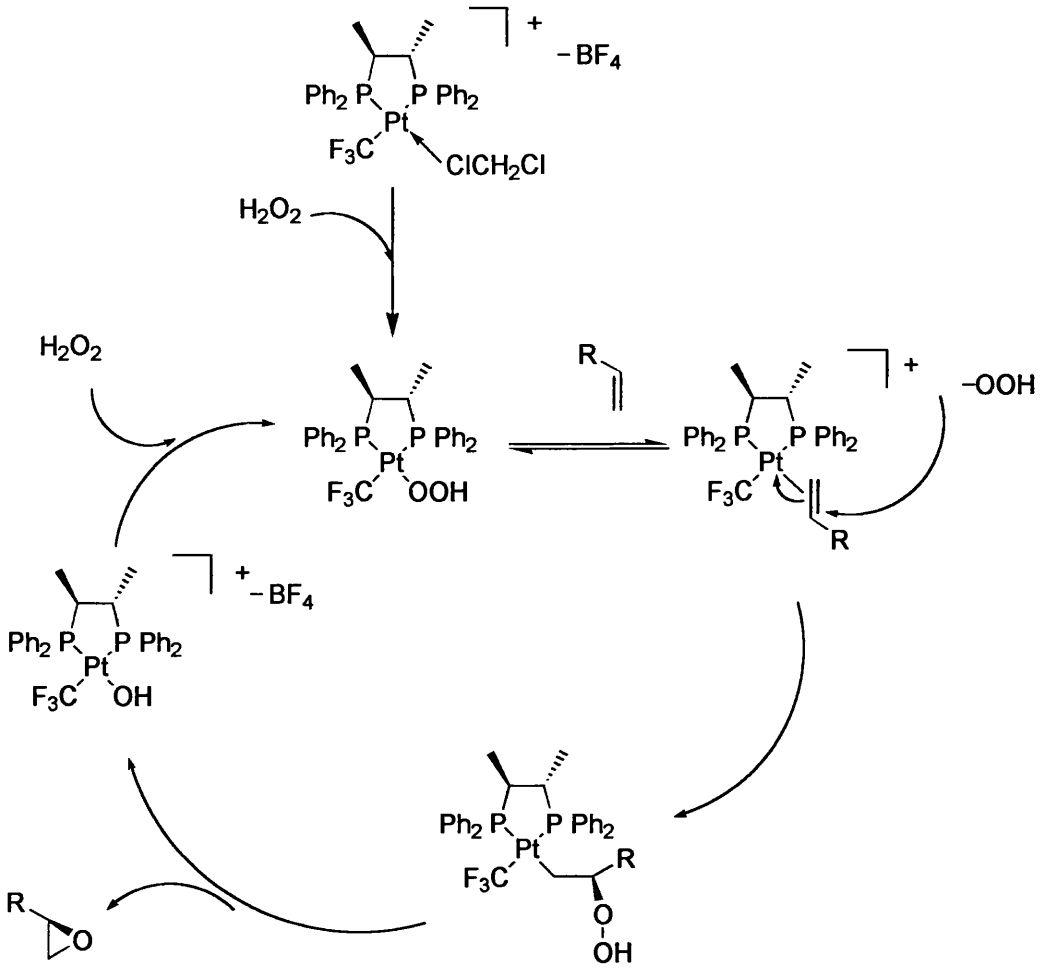


Fig. 2.4 Proposed mechanism for platinum catalysed epoxidation of alkenes

The key to obtaining high enantioselectivity in this process is to design a platinum complex which can selectively bind one prochiral face of the terminal alkene. A terminal alkene binding to a metal centre in an η^2 fashion can position its alkyl or aryl chain in one of four quadrants of space. If three out of four of these quadrants can be blocked off by other ligands on the metal, then it should be possible to develop a highly enantioselective reaction. By making one possible alkene environment more favourable than the other three, it is anticipated that the rate of nucleophilic attack will be greater for the favoured complex. As there are other reactions which involve a nucleophilic attack on an alkene, a metal complex which

can selectively bind one face of an alkene and activate it to nucleophilic attack would be of considerable interest.

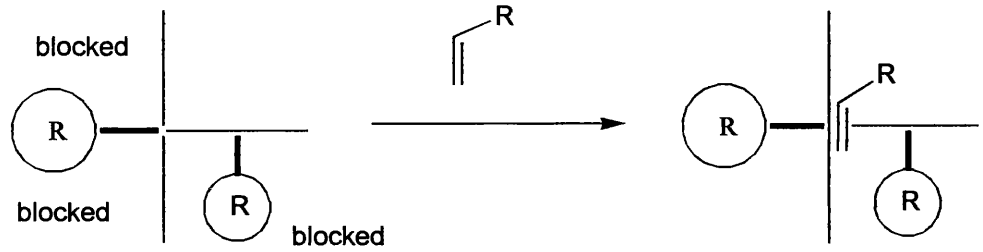


Fig. 2.5 Ideal co-ordination environment for enantioface binding of a terminal alkene

In recent years, there have been a number of enantiopure ligands designed which can direct their chirality towards the co-ordination sites on the metal. A prominent example of such a ligand is the phosphino-oxazoline ligand **(64)**.[55] Complexes of such a ligand should provide a better defined environment for alkene binding. It was therefore our plan to synthesise cationic platinum complexes of type **(65)**, shown in Fig. 2.6. In the process of making complexes of the type below, we would also be studying the co-ordination chemistry of these important, heterobidentate ligands.

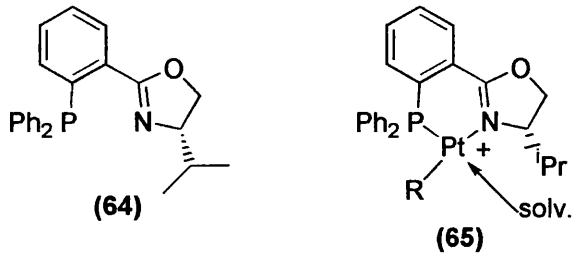


Fig. 2.6

While a compound with R = CF_3 might have the closest resemblance to the catalysts described by Strukul and co-workers, the synthesis of the precursor to these compounds, *trans*-bis-triphenylphosphine-(chloro)-trifluoromethyl-platinum

(II), is capricious and low yielding. In addition, we were concerned that the strongly bound triphenylphosphine groups might not be easily exchanged for other ligands.

We therefore sought to research whether any more readily available platinum complexes would catalyse the epoxidation and other metal mediated reactions involving alkenes. Finally, it was also realised that complexes of the type in Fig. 2.6 might also be useful for catalysing asymmetric reactions of other substrates by acting as a chiral Lewis acid.

2.2 Synthesis and characterisation of new divalent platinum complexes of (4S)-2-(2-diphenylphosphinophenyl)-4-isopropyl-1,3-oxazoline.

As our starting point, we chose to prepare complex **(66)**. This simple compound could be used to answer a number of questions we asked ourselves; How does ligand **(1)** (from now on abbreviated as (*S*)-P^N bind to platinum? Can complex **(66)** be used as a starting material for other useful complexes? Would it be possible to remove a chloride ion from **(66)** and replace it with an alkene? Does it catalyse the epoxidation reaction in its own right?

Our initial attempts to prepare [(*S*)-P^N]$PtCl_2$, **(66)** by ligand exchange from *cis*-bis(triphenylphosphine) platinum(II)dichloride failed entirely under a variety of conditions, giving back unreacted starting material. It seems that the triphenylphosphine ligand is not sufficiently labile to be replaced by the oxazoline ligand despite the process probably being favoured entropically (there are more bits

at the end). The desired compound, **(66)** is successfully prepared by refluxing the phosphino-oxazoline ligand and K_2PtCl_4 in acetonitrile.

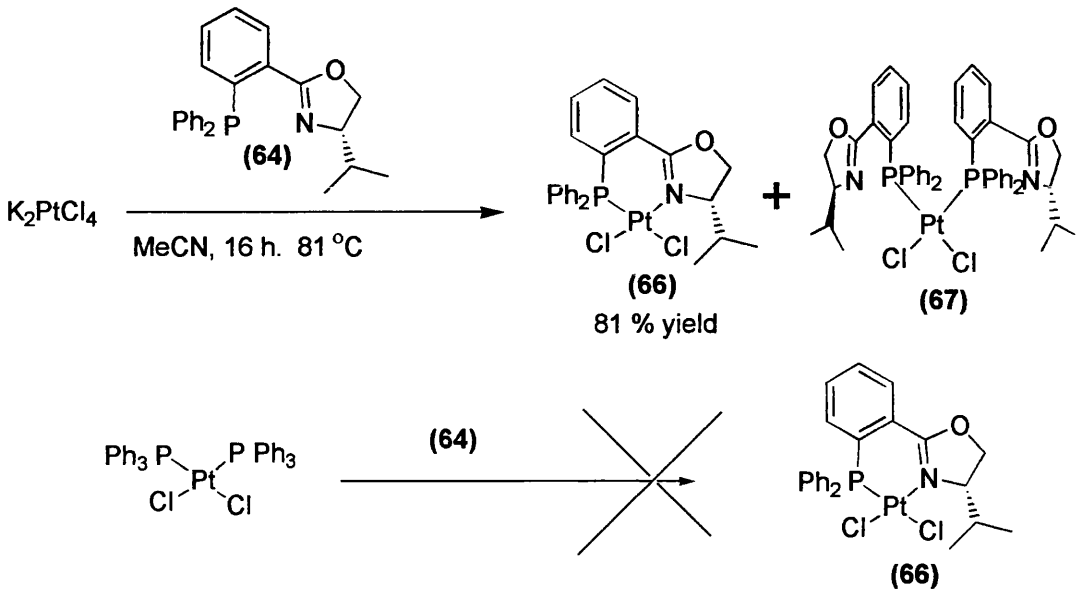


Fig. 2.7

The crude product from this reaction contains two phosphino-oxazoline complexes. ^{195}Pt NMR was useful in assigning the identity of these; Compound **(66)** showed a doublet as there is only one phosphorus atom bonded to the metal in η^2 bidentate fashion, while compound **(67)** gives a triplet, representative of the two chemically identical phosphorus atoms that are bound via an η^1 monodentate co-ordination mode. The ligands in compound **(67)** can be assigned as being *cis* to each other by ^{31}P NMR. [The size of the coupling constant between phosphorus and platinum depends on the trans influence of the ligand *trans* to phosphorus. Thus, if a phosphorus ligand is bound *trans* to a ligand of low trans influence such as chloride the platinum-phosphorus bond is highly covalent and a large coupling constant results].

The coupling constants, $^1J_{P\text{-}Pt}$=3722 Hz and 3410 Hz for compounds **(66)** and **(67)** respectively are typical of phosphines bound *trans* to a chloride.

Phosphine ligands that are bound *trans* to a ligand of high trans influence have significantly smaller coupling constants. For example, phosphines bound *trans* to each other typically have $^{1}J_{P\text{-}Pt}$=1500-2500 Hz. Fortunately, compounds **(66)** and **(67)** are readily separable by flash chromatography. Using the procedure described in the experimental, pure [(*S*)-P^N]$PtCl_2$ can be isolated in 81 % yield.

We attempted to prepare a platinum alkene complex from compound **(66)**. We therefore treated it with one equivalent of silver tetrafluoroborate in dichloromethane, filtered off the AgCl precipitate, and then added 1-octene. We recorded the NMR spectra of the product prior to addition of the alkene, the octene itself, and the product formed from mixing alkene and platinum complex together. Analysis of the NMR spectra showed no interaction between alkene and platinum.

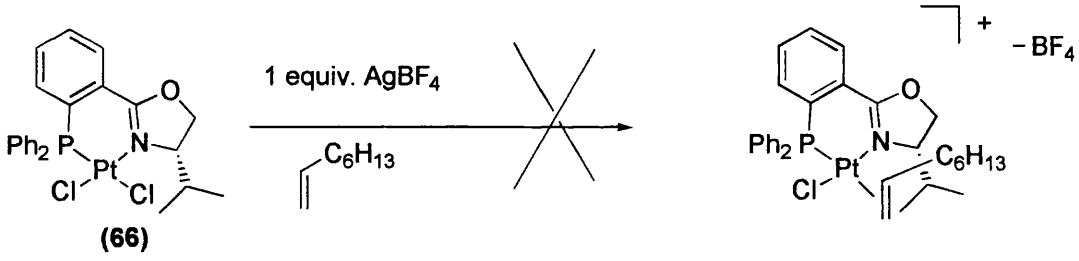
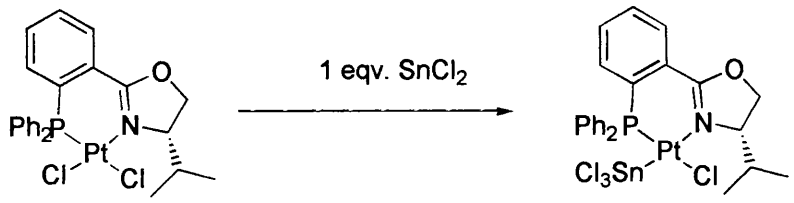


Fig. 2.8 Attempted preparation of a platinum alkene complex

It was thought that **(68)** (shown in Fig. 2.9) may provide a similar electronic environment as a trifluoromethyl complex. It was therefore prepared by the route shown. It is interesting that the trichlorostannyl ligand is selectively positioned *trans* to the nitrogen atom. The chloride *trans* to phosphorus is expected to be kinetically more reactive due to the trans effect.

The complete selectivity of this process can be assigned using ^{31}P NMR, by comparison with work on bis-phosphine complexes.[56] ^{31}P NMR of a platinum

compound containing the trichlorostannyl ligand should show a phosphorus signal, platinum "satellites" due to the 33% abundance of the NMR active ^{195}Pt nuclei, and also tin satellites due to the presence of the NMR active ^{119}Sn and ^{117}Sn nuclei.

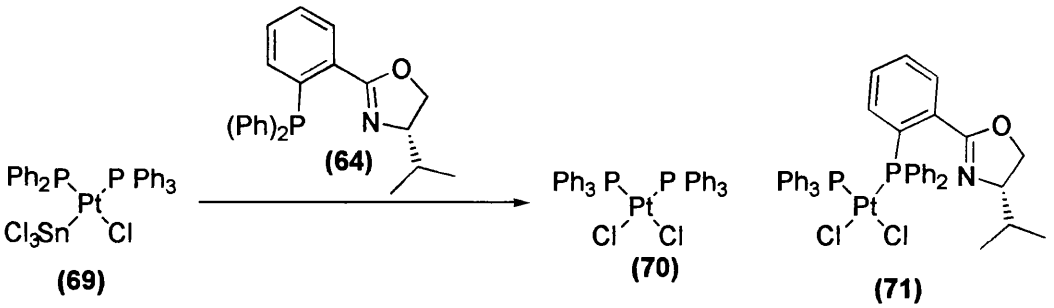


(66) (68)

Fig. 2.9

It has been shown that the magnitude of $^{2}J_{P\text{-}Sn}$ depends strongly on whether the two nuclei are *cis* (150-200 Hz) or *trans* (2100-2400 Hz). In addition, $^{1}J_{P\text{-}Pt}$ is smaller when the phosphorus atom is *trans* to $SnCl_3$. Our experimental data ($^{1}J_{P\text{-}Pt}$=3541 Hz, $^{2}J_{P\text{-}Sn}$= 156 Hz) shows fairly conclusively that the $SnCl_3$ ligand is co-ordinated *cis* to the phosphine.

We initially tried to prepare complex **(68)** by a phosphine exchange route from *cis*-bis-(triphenylphosphine)-chloro-(trichlorostannyl)-platinum (II).[56] In this case we again used ^{195}Pt and ^{31}P NMR to deduce that this exchange reaction had again not gone according to plan. The products isolated were probably a mixture of compounds **(70)** and **(71)**.



(64) (69) (70) (71)

Fig. 2.10 Triphenylphosphine ligands are not displaced by ligand (64)

It was hoped that treatment of complex **(68)** with $AgBF_4$ would release a vacant co-ordination site, and hence give a Lewis acidic cationic complex. However, this reaction always resulted in decomposition. Although it was not possible to prepare a cationic complex by the route shown in Fig. 2.11, we felt the platinum-tin bimetallic compounds may still have catalytic properties, as it has been shown that simply mixing $(LL)PtCl_2$ type compounds with $SnCl_2$ generates complexes which interact with alkenes. This combination is the most commonly used hydroformylation catalyst.

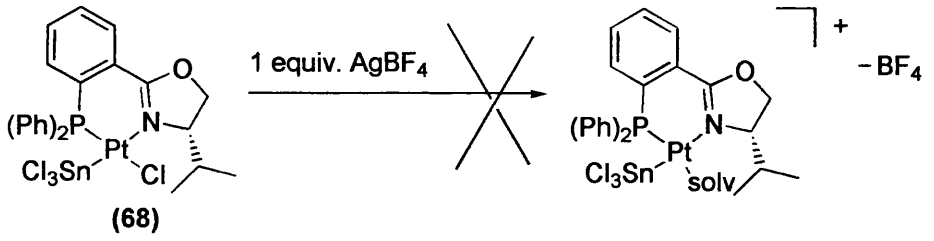
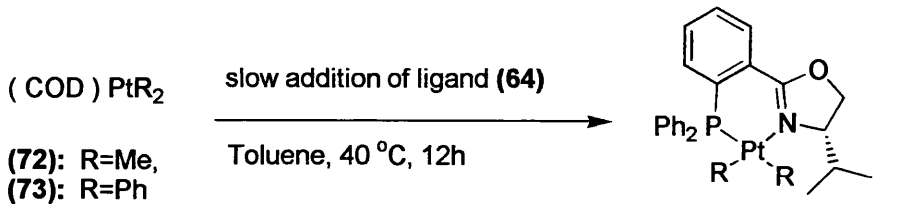


Fig. 2.11 Complex (68) decomposes in the presence of silver salts

The dimethyl and diphenyl derivatives, **(74)** and **(75)** were prepared by ligand displacement reactions from readily available $(COD)PtR_2$ (Fig 2.12).[57] The ^{31}P NMR spectra of these two compounds showed the characteristic small coupling constants ($^1J_{P\text{-}Pt}$= 1972 and 1849 Hz respectively) associated with strongly bound *trans* alkyl or aryl ligands.[58]

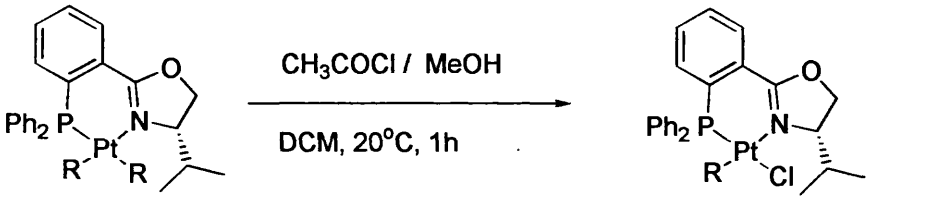


(74): R=Me; yield = 98%

(75): R=Ph; yield = 65%

Fig. 2.12

It was hoped that the selective cleavage of the Pt-C bond *trans* to phosphorus could be achieved. This would enable the vacant co-ordination site to be generated in the chiral pocket created by the oxazoline ring. As it turns out, addition of 1.1 equivalents of HCl (generated by methanolysis of acetyl chloride) gives single isomers of compounds **(76)** and **(77)**. Phosphorus-platinum coupling constants [**(76)**: $^1J = 4703$ Hz; **(77)**: $^1J = 4637$ Hz] are consistent with the chloride ligand being *trans* to phosphorus. This complete selectivity is easily explained as phosphines show increased trans effect relative to nitrogen donors (Fig 2.13).

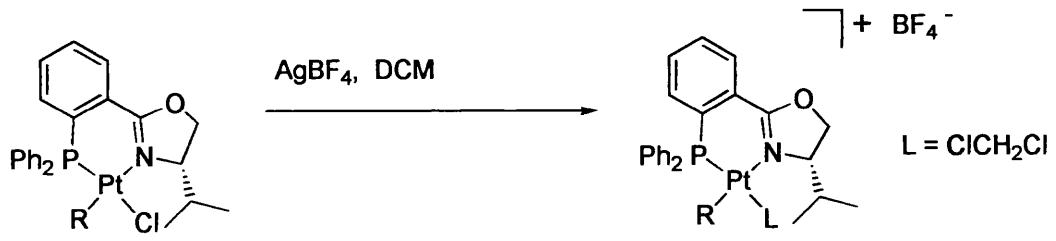


(74): R=Me
(75): R=Ph

(76): R=Me: yield = 70%
(77): R=Ph: yield = 89%

Fig. 2.13

Addition of one equivalent of $AgBF_4$ to compounds **(76)** and **(77)** gave the cationic compounds **(78)** and **(79)** (Fig. 2.14). ^{31}P and ^1H NMR spectroscopy of complex **(78)** showed the DCM ligand to be weakly bound, with the protons deshielded by the cationic platinum centre. In the case of complex **(79)**, the complex isolated was always impure, and was therefore not fully characterised. However, the spectroscopic data obtained confirmed that chloride abstraction had taken place, giving a cationic compound which contained weakly bound ligands. It seems most likely that compound **(79)** is a mixture of the desired DCM solvento complex and an aquo complex.



(76): R=Me

(77): R=Ph

(78): R=Me: yield = 90%

(79): R=Ph: yield = 90%

Fig. 2.14 Formation of cationic solvento- complexes

As a potential route to organoplatinum complexes similar in structure to complexes **(76)** and **(77)**, we carried out the carbene insertion of ethyl diazoacetate with [(*S*)-P^N]$PtCl_2$ (Fig. 2.15). It was hoped that this insertion would proceed regioselectively to produce complex **(80)**. This reaction with (chiral diphosphine)$PtCl_2$ complexes has been investigated by Bergami, Pringle and co-workers.[59] They found that diastereoselectivity could be obtained in the insertion step, and through crystallisation prepared single diastereomers of the insertion product. The chiral α-carbon atom is configurationally stable, and diastereomer ratios can be measured by ^{31}P NMR spectroscopy.

A solution of [(*S*)-P^N]$PtCl_2$ in $CDCl_3$ was treated with five equivalents of ethyl diazoacetate. All of the starting material was converted into a single new product. However, ^{31}P NMR spectroscopy showed two signals of roughly equal intensity 0.1 ppm apart (assigned as a 50:50 mixture of the two diastereomers). Unfortunately, the platinum-phosphorus coupling constant ($^{1}J_{P\text{-}Pt}$=2230 Hz) is indicative of the newly formed Pt-C bond being *trans* to phosphorus, and hence not suitable for the preparation of complexes of type **(65)**. As a result of this, no further characterisation was carried out.

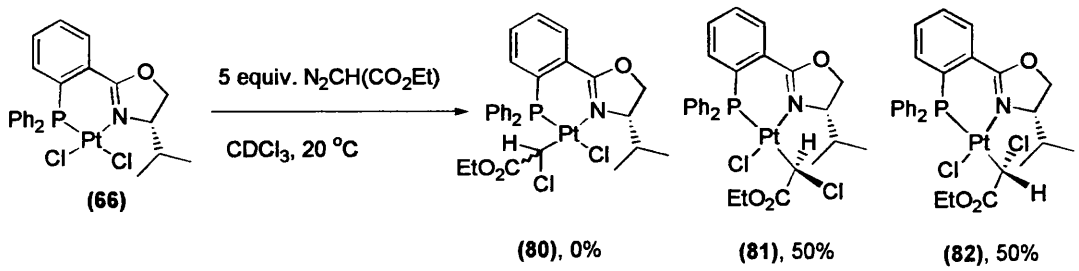


Fig. 2.15 Insertion of ethyl diazoacetate into the Pt-Cl bond of complex (66) is chemoselective, but gives a diastereomeric mixture of the unwanted isomer

We have also prepared an impure sample of what is assumed to be [(*S*)-P^N]Pt(C_6F_5)I, **(84)**. The problem with this synthesis was the preparation of cyclo-octadiene precursor **(83)** which was obtained in low yield and purity (formation of complex **(83)** is known to be inefficient).[8] After displacement of the labile COD ligand by **(64)** we obtained a yellow powder which was probably the desired compound, **(84)** (^3J = 4205 Hz) with a considerable amount of the diiodo derivative as impurity (^3J = 3979 Hz). The compound was never purified or fully characterised.

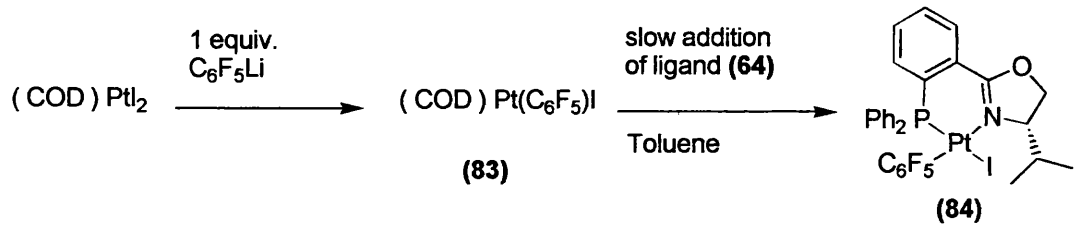


Fig. 2.16

Crystal structure of complex (75).

As our aim at this stage of the game was to prepare complexes that would have the general shape shown in Fig. 2.5, it was of considerable interest to determine the crystal structures of some of the complexes.

Single crystals of [(*S*)-P^N]$PtPh_2$, **(75)** were obtained from DCM / petroleum ether (60/80) after standing at room temperature overnight. An ORTEX [60] view of the structure is shown in Fig. 2.17, along with selected bond lengths and angles in Table 2.1. The structure shows some deviation from idealised square planar geometry. The bite angle of the bidentate ligand, N(1)-Pt(1)-P(1) is 85.7°. In the crystal structure of [(*S*)-P^N]$PtCl_2$, (see Chapter 3) this bite angle is exactly 90°.

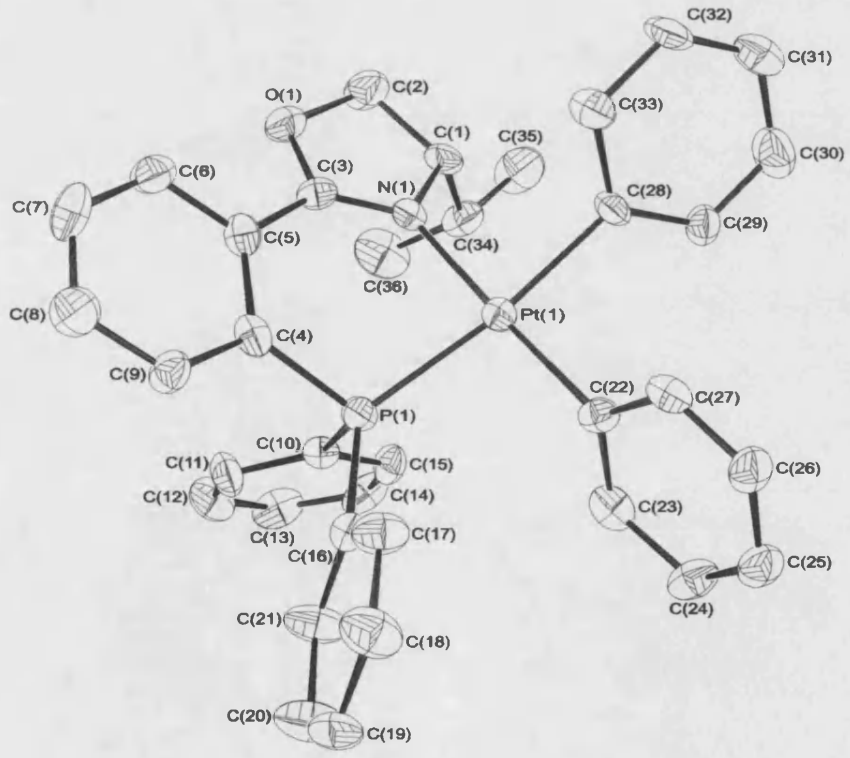


Fig. 2.17 Crystal structure of [(*S*)-P^N]$PtPh_2$

Table 2.1. Selected bond lengths [Å] and angles [°] for [(*S*)-P^N]$PtPh_2$, **(75).**

Pt(1)-C(22)	2.006(13)	C(10)-P(1)-Pt(1)	116.5(4)
Pt(1)-C(28)	2.050(12)	C(3)-N(1)-C(1)	107.6(12)
Pt(1)-N(1)	2.086(11)	C(3)-N(1)-Pt(1)	129.6(10)
Pt(1)-P(1)	2.289(3)	C(1)-N(1)-Pt(1)	122.8(8)
P(1)-C(4)	1.813(14)	C(3)-O(1)-C(2)	107.0(11)
P(1)-C(16)	1.824(14)	N(1)-C(1)-C(34)	112.2(11)
P(1)-C(10)	1.825(11)	N(1)-C(1)-C(2)	102.8(12)
N(1)-C(3)	1.30(2)	C(34)-C(1)-C(2)	114.0(14)
N(1)-C(1)	1.49(2)	O(1)-C(2)-C(1)	104.7(12)
O(1)-C(3)	1.36(2)	N(1)-C(3)-O(1)	115.6(13)
O(1)-C(2)	1.45(2)	N(1)-C(3)-C(5)	128.3(13)
C(1)-C(34)	1.51(2)	O(1)-C(3)-C(5)	116.1(12)
C(1)-C(2)	1.52(2)		
C(3)-C(5)	1.47(2)		

This contraction probably opens out the co-ordination sphere to accommodate the two phenyl ligands. The angle between the diphenylphosphino moiety and the phenyl group co-ordinated *cis* to it [C(22)-Pt(1)-P(1)=96.9°] is large, hence reducing interactions between P-aryl and Pt-aryl rings. This is not the case with the phenyl ring *cis* to the oxazoline moiety; C(28) and N(1) are relatively close together [C(28)-Pt(1)-N(1) = 88.6°]. This is possible because the phenyl ring relieves any steric clashes by orientating itself above the plane of the molecule , w.r.t. the isopropyl group C(34)-C(35)-C(36) [C(28)-Pt(1)-P(1) =171.8°]. This significant deviation is a manifestation of the chiral centre at C(1), and is one of several effects throughout the structure brought about by this single chiral carbon

atom; The ligand and platinum form a six membered chelate ring which is puckered, with all three carbon atoms residing above the plane of the complex. As has been found with a crystal structure of a palladium complex of this ligand,[61] the phenyl groups from the diphenylphosphino moiety adopt a face-on / edge-on conformation. (The edge-on phenyl group is below the plane of the complex). This ligand can therefore transmit chiral information from both sides of the ligand.

Crystal structure of [(*S*)-P^N]Pt(Me)Cl, (76).

Single crystals of **[(*S*)-P^N]Pt(Me)Cl, (76)** were grown from DCM/ petroleum ether (60/80). However, as revealed by elemental analyses and the electron density map from the diffraction experiments, the crystals contained petroleum ether. These disordered solvent molecules hampered the solution of the structure (further details are described in Appendix 1).

As a result of this, the structural parameters have relatively large standard deviations. Although no quantitative data can be obtained from the bond lengths, the overall structural features are not invalidated. An ORTEX [60] view of the structure is shown in Fig. 2.18, along with selected bond lengths and angles in Table 2.2.

Table 2.2. Selected bond lengths [Å] and angles [°] for [(*S*)-P^N]Pt(Me)Cl, **(76).**

Pt-C(1)	2.12(2)	C(1)-Pt-N(1)	177.3(7)
Pt-N(1)	2.13(2)	C(1)-Pt-P(1)	94.1(7)
Pt-P(1)	2.181(4)	N(1)-Pt-P(1)	87.8(7)
Pt-Cl(1)	2.352(5)	C(1)-Pt-Cl(1)	87.5(7)
P-C(17)	1.792(14)	N(1)-Pt-Cl(1)	90.7(7)
P(1)-C(10)	1.80(2)	P(1)-Pt-Cl(1)	178.4(8)
P(1)-C(11)	1.85(2)	C(17)-P(1)-Pt	115.8(5)
N(1)-C(4)	1.28(3)	C(10)-P(1)-Pt	112.1(6)
N(1)-C(2)	1.55(3)	C(11)-P(1)-Pt	115.7(9)

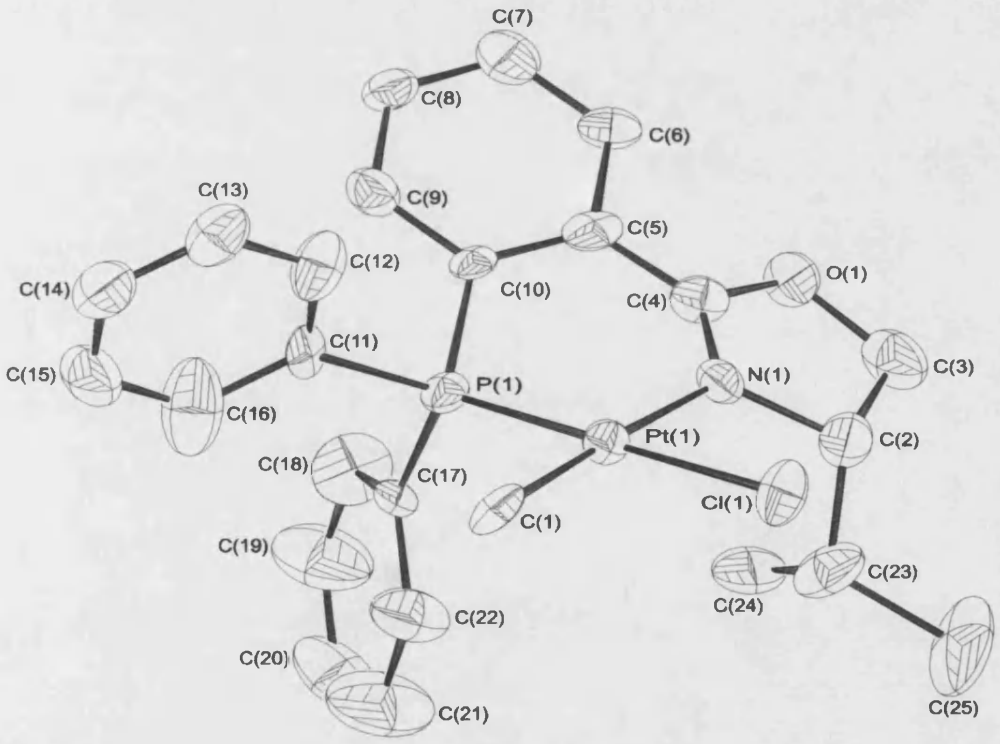


Fig. 2.18 Crystal structure of [*(S)*-P^N]Pt(CH_3)Cl

The structure does confirm NMR data which assigned the chlorine atom as being trans to the phosphorus atom. The conformation of the phosphino-oxazoline ligand is very similar to that in the diphenyl complex, although the bite angle of the ligand is slightly larger [N(1)-Pt(1)-P(1) = 87.8°]. The complex shows less deviation from square planar geometry compared to complex **(75)**. The chlorine atom is not forced up and away from the isopropyl group [P(1)-Pt(1)-Cl(1) =178.4°], and the methyl and chlorine groups do not push each other apart [C(1)-Pt(1)-Cl(1) = 87.5°]. The structure does show the bulk features outlined in Fig. 2.5. The achiral organic ligand and the chiral oxazoline are situated as desired, and should exert an influence at this site.

2.3 Catalysis

2.3a Epoxidation

The test reaction we chose to study was the epoxidation of 1-octene with 35% hydrogen peroxide, using DCM as solvent and about 2 mol% of the platinum catalyst (Fig. 2.20). These conditions were identical to those published with Strukul's catalysts.[47]

Gas chromatography was used to detect any conversion of octene to epoxyoctane. This analytical method was sufficient to detect down to 1% conversion. Catalytic experiments and a control were set up, each under identical conditions, as described in the experimental. The following complexes were tested:

Complex **(66)**

Complex **(66)** in the presence of $AgBF_4$

Complex **(66)** in the presence of $SnCl_2$

Complexes **(78)** and **(79)**

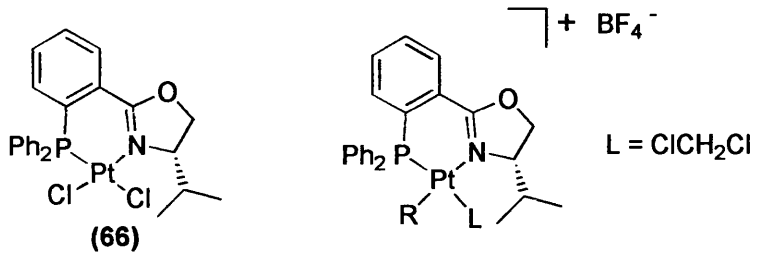


Fig. 2.19

Each reaction was analysed by G. C. after 4, 24, and 72 hours. There was no epoxide detected in any of these cases. There was also no sign of any other products. $[(S)\text{-P^N}]Pt(CH_3)CH_2Cl_2]BF_4$ was also tested as a catalyst using NaOOH as oxidant (as the acidity of the reactions above could be decomposing the platinum complexes). However, there was still no sign of products.

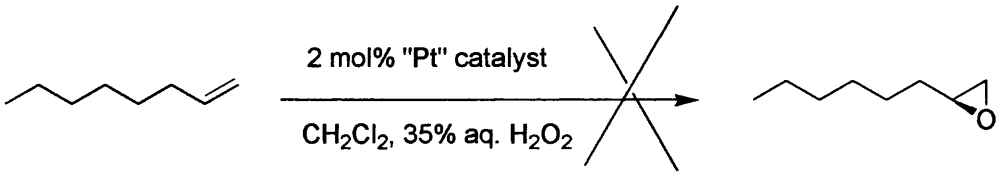


Fig. 2.20 None of the platinum complexes we prepared catalysed epoxidation of 1-octene

2.3b 1,3-Dipolar cycloadditions

An alternative reaction involving a nucleophilic attack on an alkene is the 1,3-dipolar cycloaddition reaction of nitrones.[62, 63] The products from these reactions are of synthetic importance as they can be readily converted into 1,3 amino alcohols (Fig. 2.21).

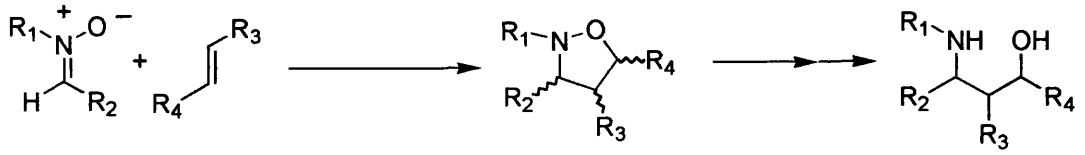
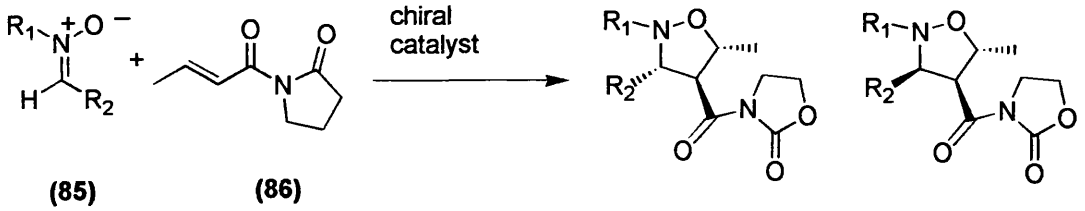


Fig. 2.21

Enantiopure metal complexes have been reported to catalyse this reaction, but only if substrates of type **(86)**, which contain additional functionality, are used.



(85) **(86)** **(87)**, *endo* **(88)**, *exo*

Fig. 2.22

There have been several attempts at making the above reaction diastereo- and enantioselective and these have been reviewed.[63] Palladium complexes give e.e.'s up to 91 %, but relatively poor endo/exo selectivity.[64] A ytterbium catalyst derived from (S)-BINOL, $Yb(OTf)_3$, and a chiral amine requires rather large amounts of catalyst (20 mol% of each component) but gives endo/exo selectivity of 99:1 and up to 96 % e.e.[65]

We wondered if our platinum complexes would catalyse the 1,3-dipolar cycloaddition reactions of unfunctionalised alkenes. We hoped that the alkene would donate electrons to the platinum cations hence lowering the energy of its lowest unoccupied molecular orbital, and speeding the reaction up. The reaction shown in Fig. 2.23 was chosen as our test reaction.

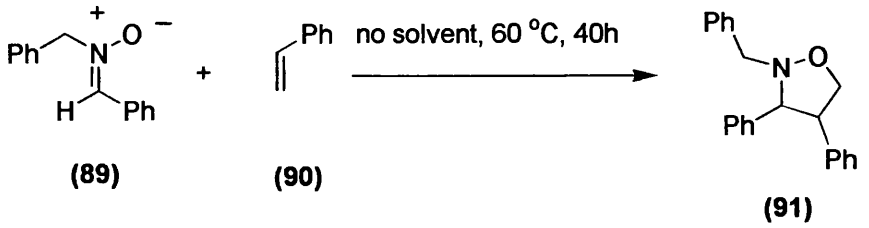


Fig. 2.23

The product, **(91)** was prepared by the literature route (Conditions: 40 hrs @ 60 °C, styrene as solvent).[66] If the reaction was carried out at room temperature using DCM as solvent, no product was detected. Sadly, this is still the case in the presence of [(*S*)-P^N)Pt(CH_3)CH_2Cl_2]BF_4, **(78)**. Under all conditions tested the cationic platinum complex **(78)** failed to catalyse the reaction. It seems likely that nitrone, **(89)** is too good a ligand even for oxophobic platinum complexes, and consequently the alkene is not allowed to interact with the platinum cation. Evidence for this is provided by the pronounced colour change (from pale yellow to dark red) which occurred when the nitrone was added to solutions of complex **(78)**. This colour change occurred both in the presence of the alkene, and without it. NMR spectra of this red product (**92e** in Table 2.3) remained unchanged when styrene was added.

We also briefly tested [(*S*)-P^N]Pt(CH_3)CH_2Cl_2]BF_4, **(78)** as a catalyst for the aza Diels-Alder reaction [67] of Danishefskys diene [68] with an imine. However we did not observe any of the desired products.

2.3c NMR studies: What can we do with our organoplatinum cations?

By way of finding out more about the vacant co-ordination site, [(*S*)-P^N]Pt(CH_3)CH_2Cl_2]BF_4, **(78)** was allowed to react with the organic ligands shown in Fig. 2.24. The ^{31}P and ^{1}H NMR spectra were then recorded, and

compared to ^{1}H NMR spectra of the free organic substrates. The results are summarised in Table 2.3.

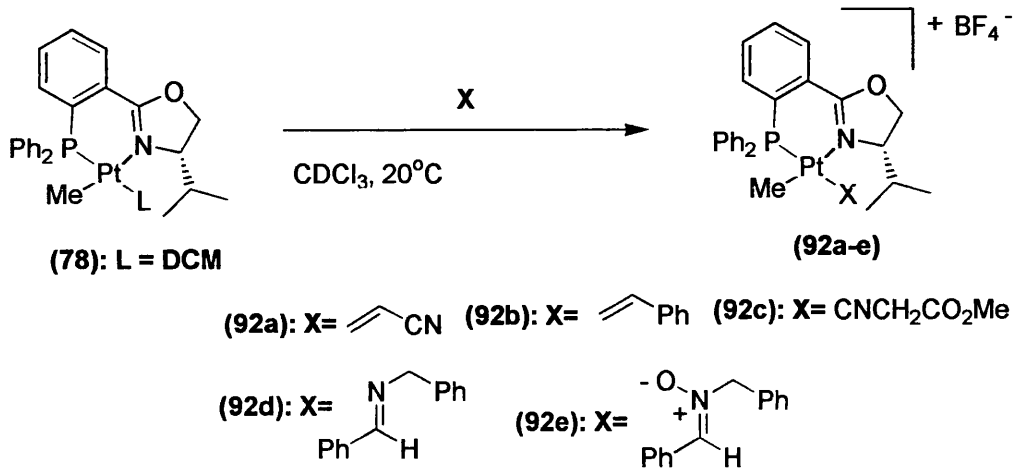


Fig. 2.24 The solvent ligand in complex (78) is easily replaced by substrates a, c, d and e

When acrylonitrile was added to a solution of complex **(78)**, a new complex formed in which the alkene protons are deshielded by the platinum cation. The smaller coupling constant, $^1J_{P\text{-}Pt}$ of the acrylonitrile complex, **(92a)**, when compared to the DCM complex, **(78)**, (4746 Hz vs. 5255 Hz) reflects the stronger interaction between the platinum cation and the acrylonitrile. A similar situation arose in the case of the methylisocyanoacetate complex, **(92c)**. When styrene, **b**, was added to a solution of **(78)** there was no change in either the ^{1}H or ^{31}P NMR spectra. The ^{1}H NMR spectrum still showed the signal attributed to co-ordinated DCM. It seems likely that styrene did not interact with the platinum cation to any great extent. The case of the imine, **d**, was somewhat more complicated. Quantitative formation of two new platinum complexes takes place. One of these can be assigned as the Pt-imine cation. The other compound present is suggested to be a benzylamine complex, formed by hydrolysis of the imine by adventitious water.

Table 2.3. Comparison of selected NMR data for free organic ligands and their metal complexes formed on addition to [(*S*)-P^N]Pt(Me)CH_2Cl_2]BF_4, **(78)**

Complex	δ_H (free substrate)	δ_H (co-ord. Substrate)	δ_P, $^1J_{P-Pt}$ in brackets
(78)	5.30	5.5	8.47 (5255 Hz)
(92a)	5.66, 6.08, 6.23	6.33, 6.53, 6.71	10.21 (4746 Hz)
(92b)	5.90, 5.84, 5.36	No change	8.47 (5255 Hz)
(92c)	3.82, 4.24	3.83, br, 4.73, br	17.57 (3424 Hz)
(92d)	4.75, 8.32	5.04, 9.51, 10.0	11.19 (4114 Hz)
			12.12 (4145 Hz)
(92e)	8.40	Many new peaks	11.49, (4350 Hz), 4.91
			(3884 Hz), 7.89
			(4919 Hz) + others

Inspection of ^{1}H NMR spectrum reveals the characteristic proton resonance of benzaldehyde. On addition of a nitrone to complex **(78)**, the NMR spectra reveal a number of new platinum complexes being formed. It seems that the nitrone decomposes in the presence of the platinum cations. We therefore felt confident that the cationic complexes would act as Lewis acids, although alkene activation did not seem likely.

2.3d Aldol reaction of isocyanoacetates with aldehydes

The formation of an isonitrile adduct by mixing [(*S*)-P^N]Pt(CH_3)CH_2Cl_2]BF_4 with ethyl isocyanoacetate suggested that this complex might be able to catalyse the asymmetric aldol reaction of isocyanoacetates with aldehydes. This reaction produces oxazoline products which are particularly useful as they can be readily hydrolysed to β-hydroxy-α-amino acids (Fig. 2.25).[19]

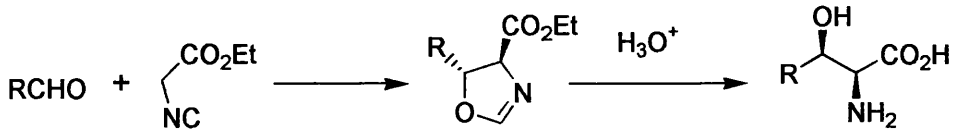
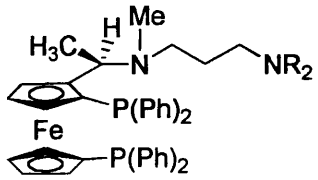


Fig. 2.25

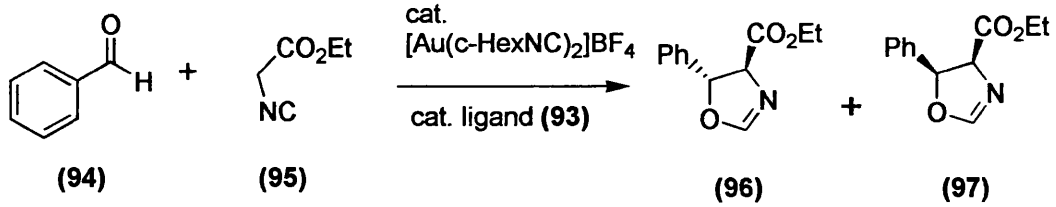
The enantiopure catalyst of choice for this reaction is a gold complex of the ferrocene derived ligand, **(93)**



(93)

Fig. 2.26

1 mol % of $[Au(c\text{-}HexNC)_2]BF_4$ in combination with the ligand, **(93)** (NR_2 = morpholine) gives quantitative yields, and excellent d.e. and e.e. (Fig. 2.27).



(94) **(95)** **(96)** **(97)**

(96) / (97) = 95:5
e.e of **(96)** = 95 %

Fig. 2.27

It is proposed that the amine substituent on the chiral ligand deprotonates the isocyanoacetate, and forms an ion pair with the ester functionality. The aldol reaction then proceeds in the very rigid co-ordination environment provided by the gold-ligand-isonitrile complex.

As already mentioned in Chapter 1, (Fig. 1.9) a platinum complex has also been shown to be a good catalyst for this reaction (although e.e. and d.e.'s are not nearly as good).[18] In the platinum catalysed reaction, the chiral ligand used is

unfunctionalised, and a catalytic amount of Hünig's base is added to the reaction to facilitate deprotonation of the co-ordinated isocyanoacetate. The platinum complex makes the isocyanoacetate protons more acidic by withdrawing electrons from the isonitrile functionality. It is this process which enables the platinum complex to speed up the reaction. However, there will still be a slight background reaction to overcome, as Hünig's base may promote the aldol reaction proceeding through unco-ordinated isocyanoacetate and an aldehyde. Richards and co-workers have found the Hünig's base catalysed reaction of substrates **(94)** and **(95)** to reach 23 % after 23 hours.[69]

We wished to establish whether our new platinum complexes would make viable Lewis acid catalysts. If complexes **(78)** or **(79)** were efficient catalysts for this reaction, an interesting possibility would be to synthesise phosphino-oxazoline ligands which contain an internal Lewis base, and to test these out in this and other reactions. It was pleasing to find that complex **(78)** did catalyse the aldol reaction of compounds **(94)** and **(95)** (Fig. 2.28). However, at the catalyst loading we used the reaction was quite slow. It is likely that any enantioselectivity observed would be eroded by the Hünig's base catalysed background reaction. The e.e. was therefore not determined.

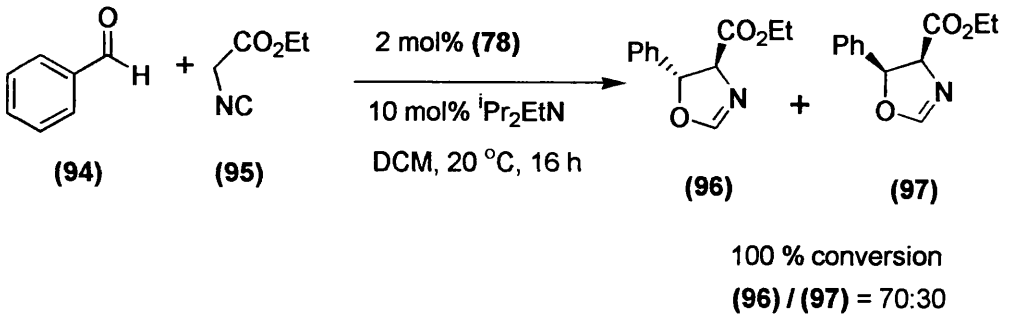


Fig. 2.28

2.3e Diels-Alder reaction of acrylonitrile derivatives

As the complexes definitely did bind, and withdrew electrons from nitrile type functionalities, we tested the complexes for catalytic activity in the Diels-Alder reaction of acrylonitrile derivatives. An enantioselective version of this reaction would be a very useful process, as the nitrile group is readily transformed into other functionalities. In the case of the 2-chloro-acrylonitrile substrate we tested, the cyano and chloro groups can be simply converted to a carbonyl group, and it therefore acts as a useful ketene equivalent.[70] Variants of this reaction have found application in a number of total syntheses.[71]

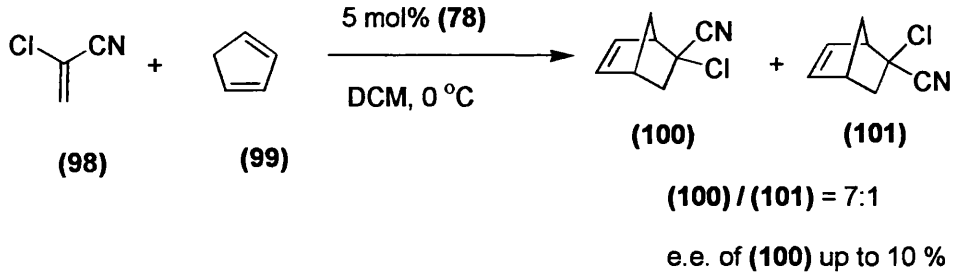
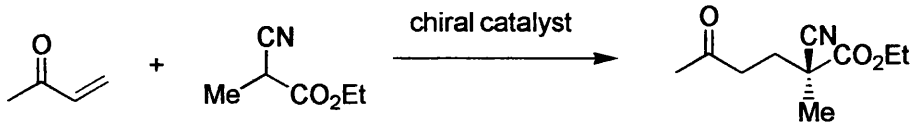


Fig. 2.29

We found that 5 mol% of complex **(78)** would catalyse the reaction shown (Fig. 2.29) to give high conversion to bicyclic compounds **(100)** and **(101)** as a 7:1 mixture of endo and exo isomers. Analysis of the NMR spectra reveals that the endo-2-chloro isomer is favoured (as is the case with the uncatalysed reaction (uncatalysed rct.: 4:1 mixture).[72] The enantioselectivity of the process could be estimated by G.C.,[73] and was always found to be low (c.10 % e.e.) under a variety of conditions. As a result of this, no further testing was carried out. This is the first time, to the best of our knowledge, that the use of an enantiopure Lewis acid has been evaluated in this reaction, and the first instance of platinum catalysing a reaction of this type. Further studies are clearly required.

2.3f Asymmetric Michael reaction of α-cyano carboxylates

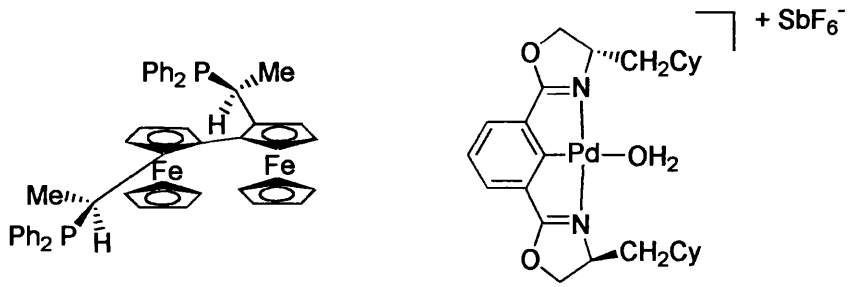
The cationic complexes were then tested as catalysts in the asymmetric Michael reaction of α-cyano carboxylates (Fig. 2.30). This reaction was first studied by Ito and co-workers.[74] They found that in the presence of 1 mol% of $Rh(H)CO(PPh_3)_3$, and the enantiopure, trans chelating ligand, **(105)**, high yields and high enantioselectivities (81 % e.e. for the substrate shown) were achieved. The high selectivities obtained using their ligand were in contrast to those obtained using "standard" chiral diphosphines.



(102) **(103)** **(104)**

Fig. 2.30

It has also been shown that this reaction proceeds in the presence of the preformed palladium catalyst, **(106)** and a catalytic amount of base to give the desired product (74% yield; 34% e.e.).[69] We wished to find out if organoplatinum cations would catalyse this reaction.



(105) **(106)**

Fig. 2.31

We were pleased to find that the methyl substituted platinum compound, [(*S*)-P^N]Pt(CH_3)CH_2Cl_2]BF_4 **(78)** was quite a good catalyst, 1 mol% of complex **(78)** giving essentially complete conversion (by T.L.C.) in 16 hours. Enantioselectivity, however, was rather low. Changing the solvent to toluene gave a small increase in e.e. The results obtained are shown in Table 2.4. In contrast, the phenyl substituted compound, **(79)**, was a much less active catalyst, with the reactions still not reaching completion even after long reaction times. This catalyst was also less enantioselective (17% e.e. vs. 25% e.e.). Although the e.e.'s obtained are relatively poor, they do suggest that changing the achiral, organic substituent could be used to fine tune the catalyst structure, without the need to prepare alternative enantiomerically pure ligands.

Table 2. 4. Asymmetric Michael reaction of ketone **(102)** and nitrile **(103)** using the new platinum complexes **(78)** and **(79)** as catalysts.

Catalyst [a]	Solvent	Rct. Time (hrs)	Yield [b]	e.e. [c] (configuration) [d]
(78) (5 mol%)	DCM	16	88 %	16 % (R)
(78)	DCM	40	78 %	17 % (R)
(78)	Toluene	16	81 %	23 % (R)
(78) [e]	Toluene	16	84%	25 % (R)
(79)	DCM	23	56 %	17 % (R)
(79)	Toluene	55	56 %	17 % (R)

a: All reactions, ran at 20 °C using 1 mol% Pt catalyst, 10 mol% Hunigs base, 1 equiv. nitrile, 1.5 equiv. methyl vinyl ketone (unless described otherwise).
b: Isolated yields by column chromatography.
c: determined by HPLC using Chiracel OD column.
d: determined by optical rotation
e: Methyl vinyl ketone added as a solution in 3 mL toluene via a syringe pump over 10 hours.

2.4 Notes on the preparation of other potential epoxidation catalysts

We next considered synthesising platinum complexes which contained other alkyl ligands. The alkyl ligand that was chosen was the powerfully electron withdrawing trifluoroacetyl ligand. A possible precursor to such a complex had previously been described.[75] We wished to have a model complex that closely resembled the original Strukul epoxidation catalysts (so we were not changing too many variables at once), so we chose to use the achiral ligand, *cis*-1,2-bis(diphenylphosphino)ethylene.

Complex **(110)**, *cis*-1,2-bis(diphenylphosphino)ethylene-chloro-(trifluoroacetyl)-platinum (II) was prepared by phosphine exchange with the known compound, *trans*-bis(methyldiphenylphosphine)-chloro-(trifluoroacetyl)-platinum (II), **(109)** (Fig. 2.32).[75]

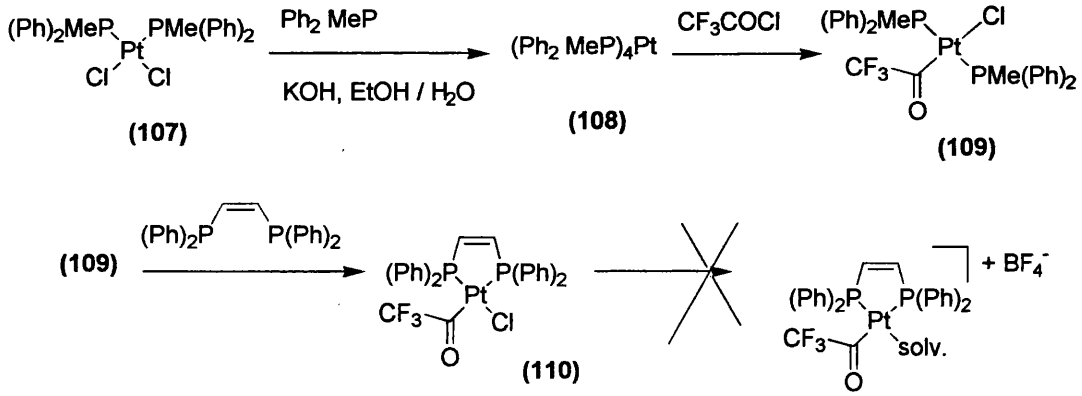


Fig. 2.32

The crude product from this reaction was always very impure and had to be purified by flash chromatography. The pure compound isolated showed the expected structure as determined by NMR. The ^{31}P NMR spectrum of this compound showed

platinum-phosphorus coupling of 1752 and 3979 Hz. The larger coupling constant attributed to the phosphorus atom trans to chloride, while the smaller coupling trans to trifluoroacetyl indicates that this group has a high trans influence. In addition to this, the two inequivalent phosphorus atoms couple to one another and to the proton in the backbone of the ligand. All our attempts to abstract a chloride ion from **(110)** using silver tetrafluoroborate resulted in decomposition (Fig. 2.32). This route to epoxidation catalysts was therefore abandoned.

Several attempts to prepare a trifluoromethyl substituted platinum complex were also made. Compound **(109)** was heated at 150 °C under vacuum (1mm Hg) to try to decarbonylate and produce *trans*-bis-(methyldiphenylphosphine)-chloro-(trifluoromethyl)-platinum(II).[75] This reaction always failed, and resulted in decomposition. Oxidative addition of CF_3Br to $(Ph_3P)_4Pt$[76] gave a complex mixture of products which we could not purify. As an alternative approach, we tried to utilise commercially available CF_3-$SiMe_3$ [77, 78] to introduce the trifluoromethyl group. However, oxidative addition of CF_3-$SiMe_3$ also gave inseparable mixtures, which were also obtained when CF_3-$SiMe_3$ was reacted with platinum(II) complexes such as $(Ph_3P)_2PtCl_2$ in the presence of tetrabutyl ammonium fluoride or other promoters.

As we did not have a route to a trifluoromethyl substituted precursor which could exchange a ligand, or ligands for the phosphino-oxazoline **(64)**, the search for epoxidation catalysts was abandoned. However, in the work I have described in the previous chapter, we learnt a lot about the co-ordination chemistry of ligand **(64)**

and prepared well defined, Lewis acidic complexes which catalysed a number of reactions. The electronic difference between the phosphorus and nitrogen donors in the ligand controls the selectivity of the substitution reactions that the platinum complexes undergo. In particular platinum-carbon bond cleavage proceeds entirely *trans* to phosphorus, insertion of $SnCl_2$ into the Pt-Cl bonds entirely *cis* to phosphorus, and insertion of diazo compounds entirely *trans* to the phosphorus donor. This selectivity could be used to prepare complexes that had many of the features we aimed for at the onset of our work (Fig. 2.6). The complexes have been shown to catalyse three different reactions using nitrile substrates. The use of platinum Lewis acid catalysts had been relatively unexplored prior to this work and may be of use in the future. While studying the Lewis acidic complexes, we became interested in using some of the compounds I had prepared as catalysts for allylic alkylation. It is this which will be discussed in the future chapters.

Chapter 3

Platinum Catalysed Allylic Substitution

3.1 Background: Transition metal catalysed allylic alkylation reactions

Allylic substitution reactions are traditionally catalysed by palladium complexes. These reactions constitute a huge area of research and have been reviewed many times.[79] The widely accepted mechanism for this reaction is shown in Fig. 3.1. A wide range of nucleophiles has been shown to be useful in the process.

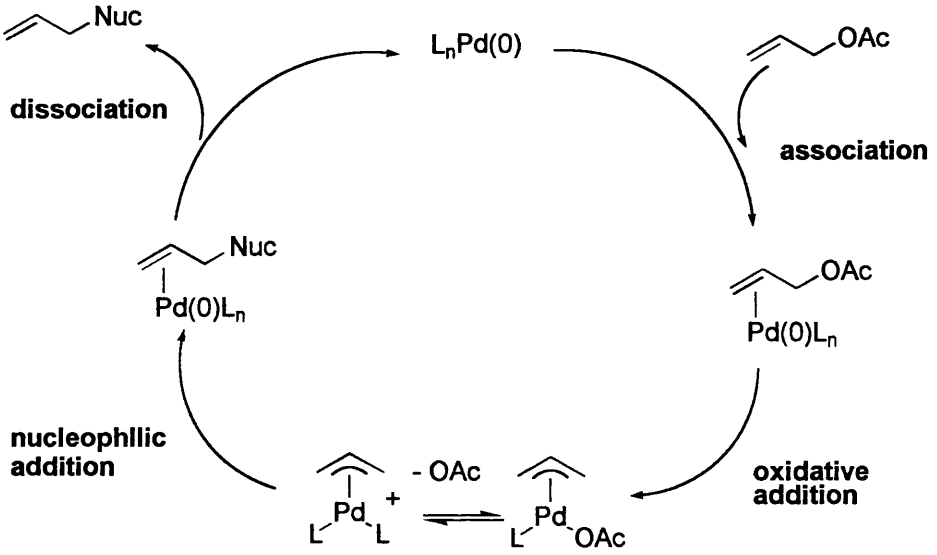


Fig. 3.1 Proposed mechanism for allylic alkylation

In order to obtain enantioselectivity when a symmetrical allylic acetate is employed, the nucleophile must attack regioselectively at one end of the allylic terminus. It took a considerable amount of time to achieve this challenge, but by the early 1990's, several research groups had achieved almost complete enantiocontrol for some symmetrical substrates such as compound **(112).** Particularly pertinent to the research described in the following chapters are the ligands of type **(111)** which were simultaneously introduced by Williams,[80] Pfaltz[10b] and Helmchen[10c]. These ligands exploit the electronic difference between the auxiliary donor atoms X and Y.

Although many different ligands of this type were prepared over the years,[81, 82, 61] the most studied ligand is [(S)-P^N], **(64).** Examples of its efficiency in palladium catalysed allylic substitution are shown below. The reaction can be used in the preparation of, for example, amino acid derivative, **(114)** and succinic acid derivative, **(117)** (Fig's 3.3 & 3.4).[80]

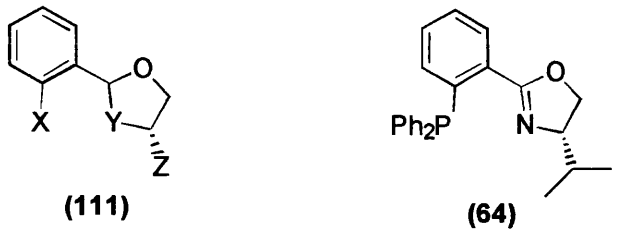


Fig. 3.2

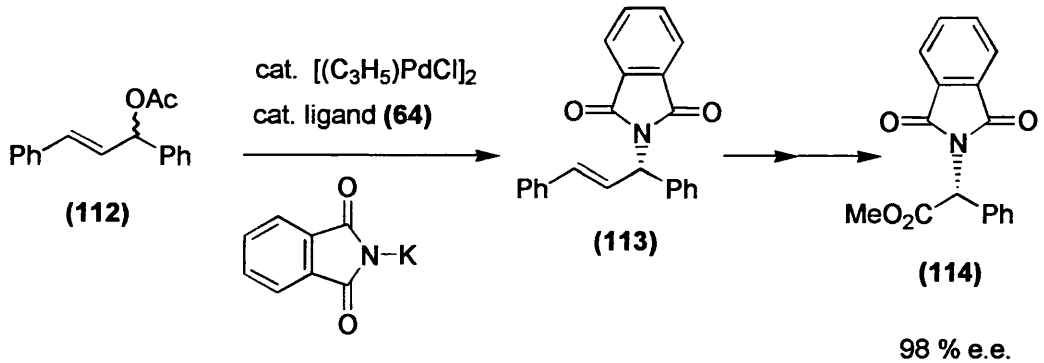


Fig. 3.3

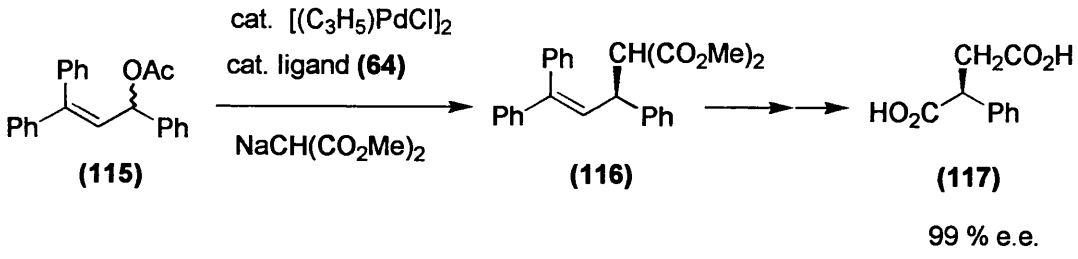


Fig. 3.4

The mechanism of enantioselective allylic alkylation when using this ligand is thought to be as follows: (Fig. 3.5)

The racemic allylic acetate oxidatively adds to the palladium. There is a kinetic resolution at this stage (one enantiomer of acetate is used up more quickly than the other). This reaction forms a pair of diastereomeric palladium allyl complexes, **(118)** and **(119)**, which are able to freely interconvert during the reaction (the rate of diastereomer interconversion is much more rapid than the rate of nucleophilic attack) The actual ratio of the two complexes **(118)** and **(119)** is 8:1.[61] Complex **(118)** is actually the favoured diastereomer.

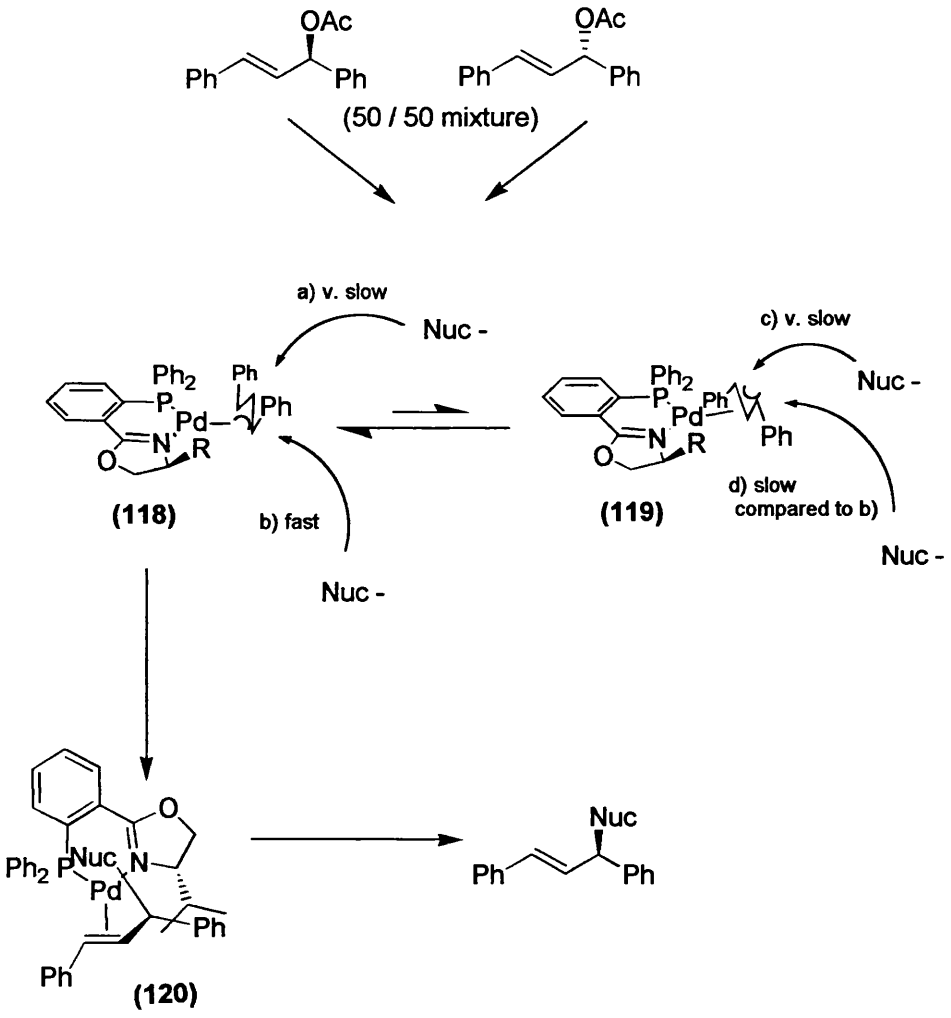


Fig. 3.5

The nucleophile then adds regioselectively *trans* to the phosphorus atom in complex **(118)** (route b) to generate the desired products *via* complex **(120)**. This is

due to the higher trans influence of the phosphorus atom activating this end of the terminus. In addition, the enantioselectivity of the products is actually greater than the ratio of diastereomeric complexes **(118)** and **(119).** It appears that the major diastereomer also reacts more quickly than the minor one. The reaction therefore proceeds almost entirely through nucleophilic attack " route" b) on complex **(118).**

Despite the usefulness of palladium catalysed allylic substitution, there are limitations in terms of substrate, nucleophile, and selectivity. Consequently, there has been ever increasing attention paid to the use of other metals that might increase the scope of the reaction. In fact, a number of important papers were published in this field during our own studies. Over the next few pages the application of a wide range of transition metal complexes as catalysts for allylic substitution will be discussed.

Palladium complexes have not been reported to catalyse allylic alkylation of Grignard reagents. Nickel complexes, however, are excellent catalysts for this transformation, and enantioselective variants of this reaction have been described.[83]

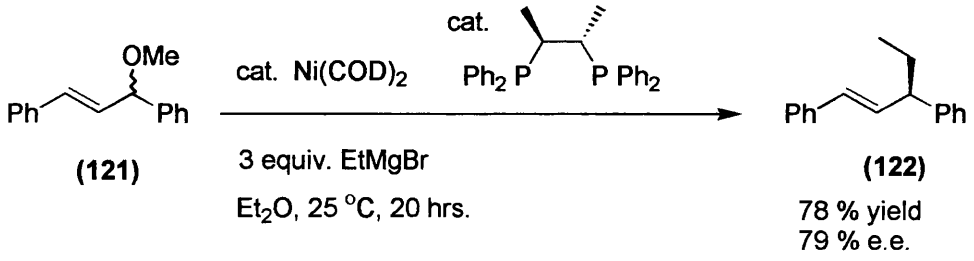


Fig. 3.6

Nickel catalysts also allow the use of aryl and alkenyl borates as nucleophiles, which are not allylated using palladium catalysts.[84] When soft nucleophiles such as dimethylmalonate are used, the highest catalytic activity is observed using

bis(aminophosphine) ligands such as ligand **(124)**. For example, when acetate **(125)** is alkylated with dimethylmalonate, the two regioisomeric products **(126)** and **(127)** are produced (B / L ~ 70 /30). The use of ligand **(124)** halves the reaction time compared to dppb, **(123),** which was previously found to be one of the best ligands for nickel catalysed allylic alkylation (Fig. 3.7). Some substrates only reacted when **(124)** was used as ligand.[85]

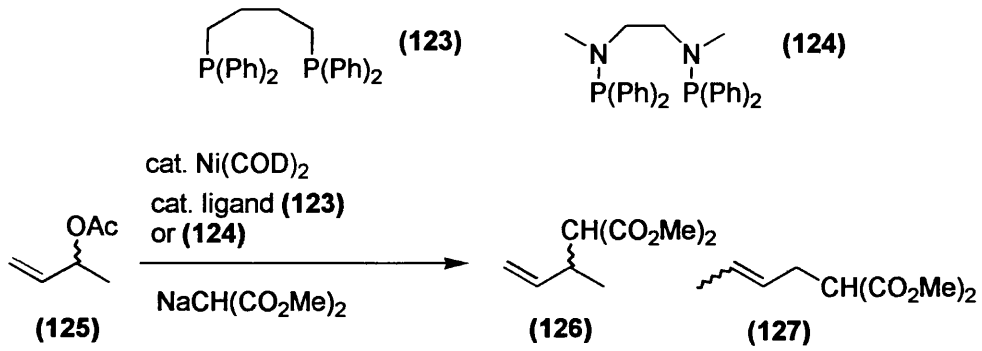


Fig. 3.7

Tungsten complexes catalyse allylic alkylation (but with lower activity than Pd) and give complementary regioselectivity to palladium: Mono-substituted allylic carbonates generally give branched products.[86] This change in regiochemical outcome, also seen with molybdenum complexes, is thought to be due to the nucleophile attacking the metal prior to nucleophilic addition to the allyl ligand. An enantioselective variant using phosphino-oxazoline complex, **(131)** has been reported.[87] Good regioselectivity and excellent e.e.'s were observed for mono-(aryl) substituted allylic phosphates such as **(128)** (Fig. 3.8).

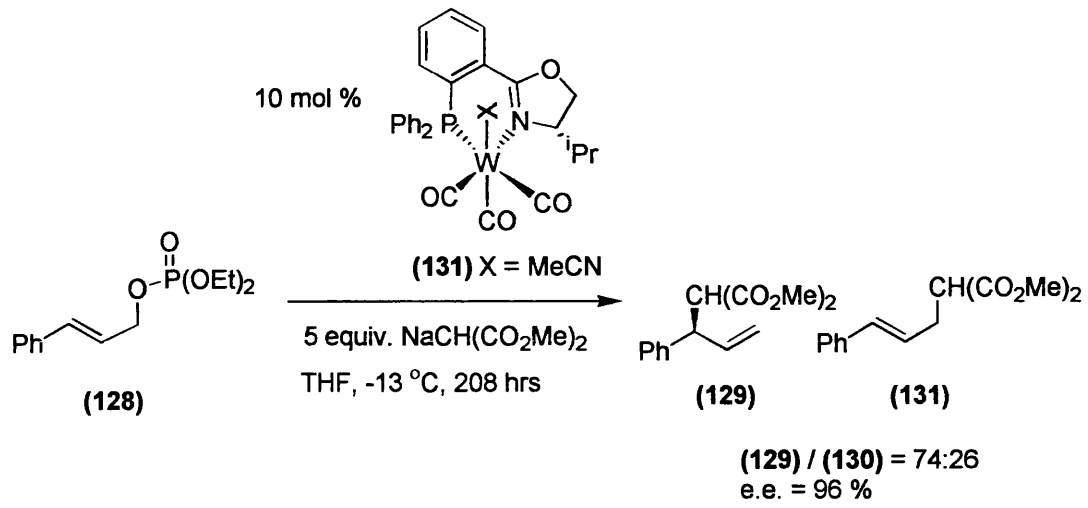


Fig. 3.8

Molybdenum catalysts are also of considerable interest. The catalysts also give the more branched isomer regioselectively from mono-substituted allylic esters.[88] Kocovsky and co-workers have shown that enol-ethers and electron rich aromatics can be allylated using molybdenum catalysis.[89] Probably the most promising example of allylic substitution catalysed by a metal other than palladium was reported while our work was in progress (Fig. 3.9). The use of a molybdenum complex of ligand **(132)** gives excellent regio- and enantioselectivity in the alkylation of carbonate **(133)**.[90] Very recently, Pfaltz and co-workers have studied similar ligands, **(134)** and **(135)** in regio- and enantioselective molybdenum catalysed allylic alkylation.[91]

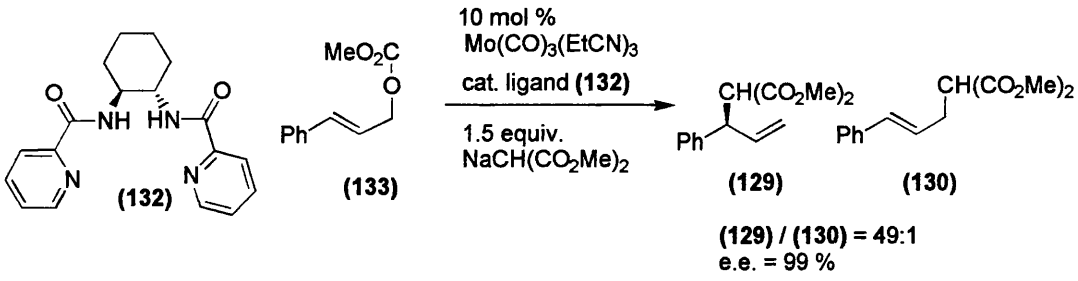


Fig. 3.9

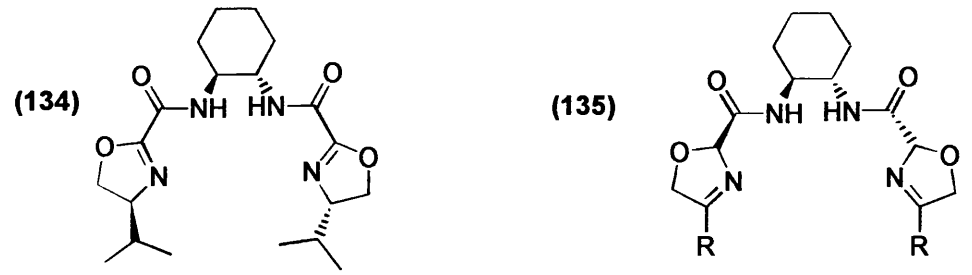


Fig. 3.10

Ruthenium complexes catalyse allylic alkylation of allylic carbonates when amines are used as solvent. The ruthenium catalysed reactions show different selectivity to palladium. Some substrate / nucleophile combinations gave mixtures of branched and linear products, whereas others gave exclusive formation of branched products and double bond isomerisation can occur under the reaction conditions. Diallylated products can also be obtained selectively when using ruthenium catalysts (Fig. 3.11).[92]

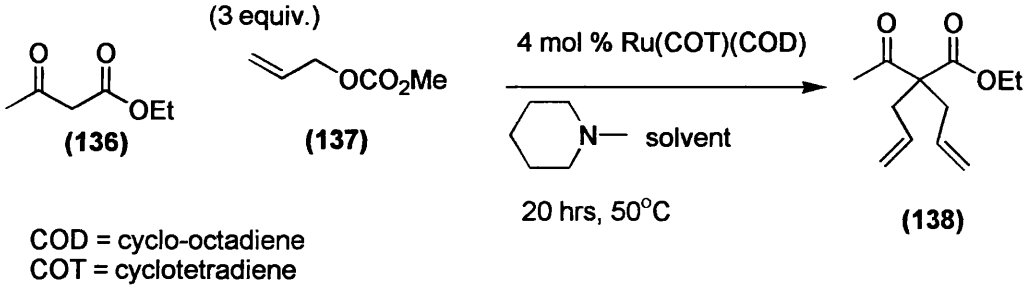


Fig. 3.11

Wilkinson's catalyst, when modified with $(MeO)_3P$ catalyses allylic alkylation. These reactions are thought to proceed via σ-allyl species, and show a memory of what the starting material was, *ie.* enantiomerically pure, branched carbonate, **(139)** gives enantiomerically pure branched product **(126)**. Linear carbonates give a mixture of linear and branched isomers (Fig. 3.12).[93]

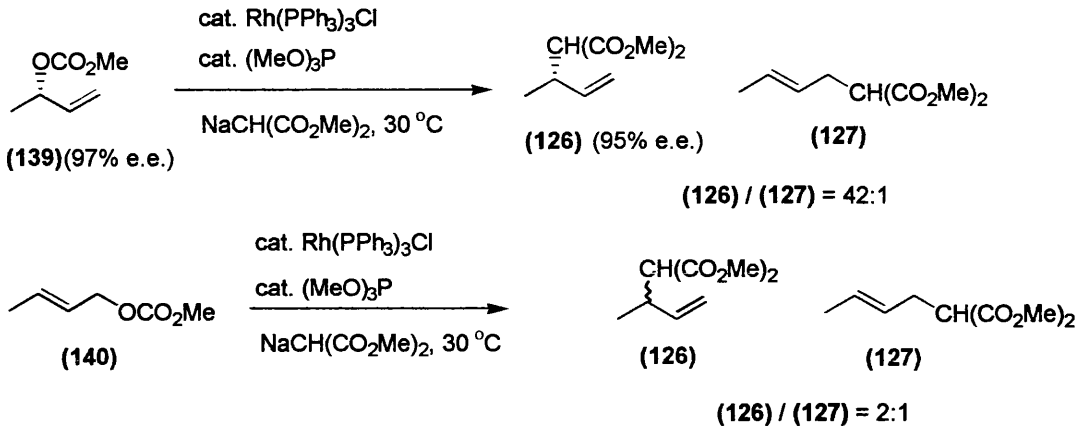


Fig. 3.12

The iridium complex $[Ir(COD)Cl]_2$, when used in conjunction with electron poor ligands catalysed allylic alkylation with excellent regioselectivity towards branched products.

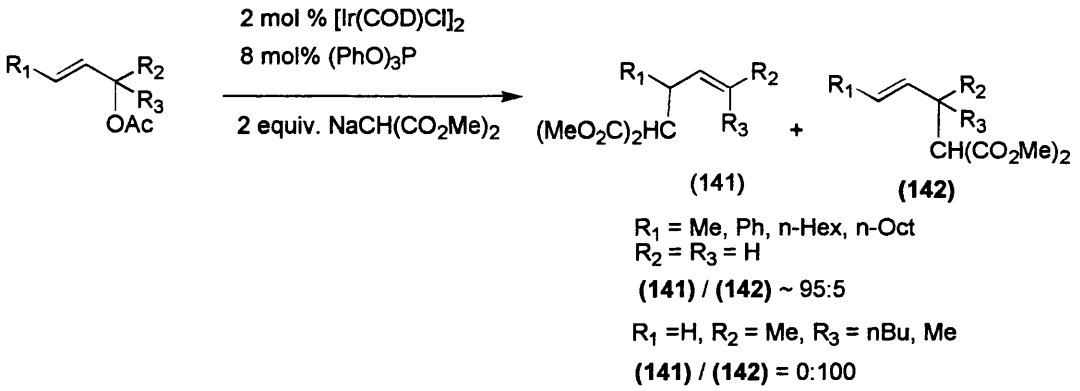
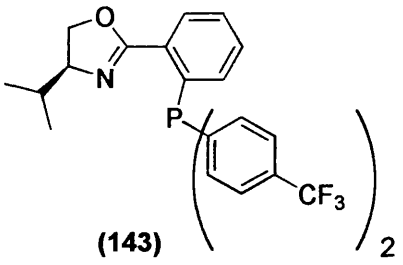
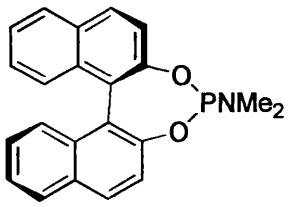


Fig. 3.13

Electron poor ligands are essential for both activity and regioselectivity, and triphenylphosphite was found to be the ideal ligand for the achiral reaction (Fig. 3.13).[94] $[Ir(COD)Cl]_2$ catalyses the reactions enantioselectively when ligands **(143)** or **(144)** are used.[95, 96]



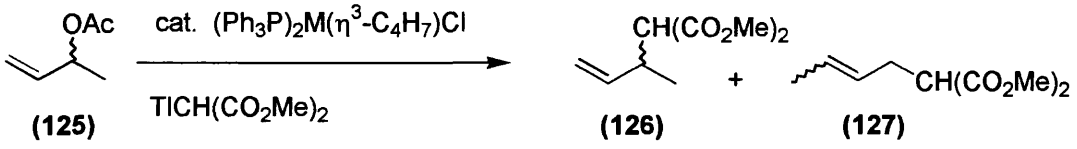
(143)



(144)

Fig. 3.14

Platinum catalysed allylic alkylations have only been reported three times in the literature. Kurosawa initially reported that $(Ph_3P)_4Pt$ catalyses allylic alkylation of allyl and butenyl acetate. Interestingly, he observed a greater proportion of compound **(126)** than could be obtained when using an otherwise identical palladium catalyst (Fig. 3.15).[97]



(125) **(126)** **(127)**

M = Pt: **(126) / (127)** = 1.5 : 1
M = Pd: **(126) / (127)** = 1 : 2.0

Fig. 3.15

Brown and co-workers also studied the reaction of butenyl acetate with sodium dimethylmalonate.[98] Labelling experiments proved that the reaction proceeds *via* nucleophilic attack on an η^3- allyl complex. The complex $[(R,R\text{-DIOP})Pt(\eta^3\text{-}C_4H_7)]BF_4$ was shown to be an interconverting mixture of all four possible isomers, **(145)-(148)** (both diastereomers for both *E* and *Z* complexes; At equilibrium *Z:E* = 1:1.7, both diasteromers in approx. equal amounts).

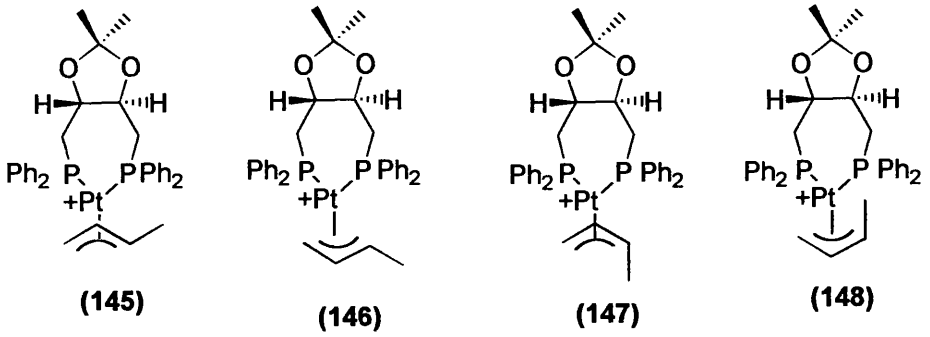


Fig. 3.16

All four of these complexes react with the nucleophile, but at somewhat different rates as the products are predominantly branched (**(126) / (127)** ~ 5:1, e.e. of **(126)** = 11%) and the linear isomer was almost entirely *E* product. The otherwise identical palladium complex [(*R,R*-DIOP)Pd(η^3-C_4H_7)]BF_4 gave lower regioselectivity towards branched product (**(126) / (127)** ~ 1.3:1, e.e. of **(126)** = 13%). A study by Murai and co-workers showed platinum complexes catalysed a double alkylation reaction.[99] This is described in greater detail in Chapter 4.

There are also reports on cobalt,[100] manganese,[101] iron,[102] and copper [103] either catalysing or stoichiometrically promoting allylic alkylation.

3.2 Results and discussion: Development of a highly enantioselective platinum catalysed allylic alkylation reaction

The aim of this area of our research was to develop a highly enantioselective allylic substitution reaction catalysed by platinum. This had never been achieved before and given the impressive advances made by studying different metals as catalysts for this reaction, we had no doubt that it could be an interesting field of study.

In particular, we wondered if the use of platinum as catalyst would give different selectivity, or allow the development of brand new types of allylation reactions.

As a starting point, we tested the readily available precursors, $(Ph_3P)_4Pt$, $(PPh_3)_2Pt$-ethylene, and $Pt(dba)_2$ [104] in the presence of the chiral ligand, (4*S*)-2-(2-diphenylphosphinophenyl)-4-isopropyl-1,3-oxazoline, **(64)** ((*S*)-P^N see Chapter 2, Fig. 2.6). The reaction chosen was the alkylation of 1,3-diphenylprop-2-enyl acetate, **(112)** with dimethylmalonate to afford product **(149)** (Fig. 3.17). This is often used as the standard reaction to assay the effectiveness of a new ligand or catalyst.

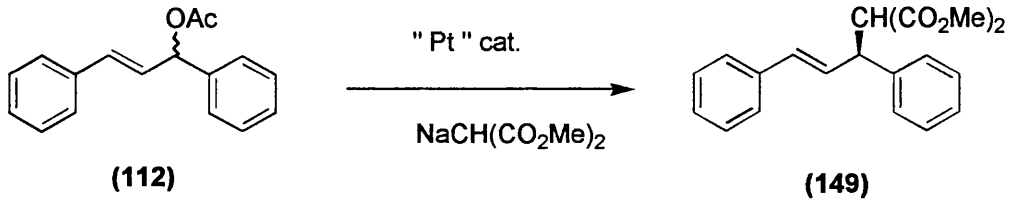


Fig. 3.17

The first two catalyst systems proceeded readily, giving complete conversion into product after 16 hours at room temperature (Table 3.1: entries 1 & 2). However, enantioselectivity is low. It is our contention that during these reactions the major catalytic species does not contain a chelating phosphino-oxazoline ligand. This is possible as the excess triphenylphosphine present could compete with the nitrogen donor of the oxazoline group for a co-ordination site on the platinum. It is assumed that (*S*)-P^N needs to chelate in order to achieve high selectivity. The low enantioselectivity is somewhat in contrast to palladium, as Gais and co-workers have successfully used a combination of $(Ph_3P)_4Pd$ and ligand **(1)** as a highly enantioselective catalyst.[105]

Attempts to characterise the platinum complexes formed when one or two equivalents of phosphino-oxazoline ligand are added to either $(Ph_3P)_4Pt$ or $(PPh_3)_2Pt$-ethylene failed.

Table 3.1. Allylic alkylation of acetate, **(112)** catalysed by readily available precursors in the presence of the ligand (*S*)-P^N.[(a)]

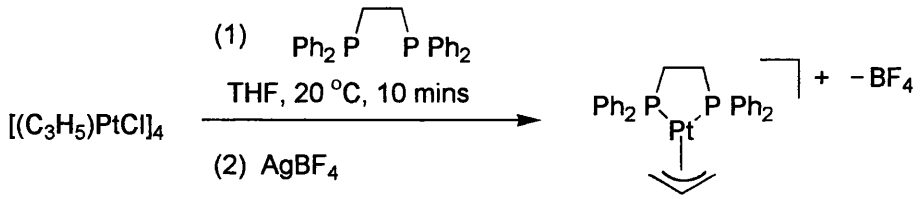
Entry	Catalyst	T / °C	t / h	yield	e. e.[(b)]
1	$(Ph_3P)_4Pt$	20	16	85	8 (S)
2	$(Ph_3P)_2Pt$-ethylene	20	16	90	28 (S)
3	$Pt(dba)_2$	20	24	trace	95 (S)
4	$Pt(dba)_2$ [(c)]	65	44	trace	(-)

a: All reactions were carried out in dry DCM using 5 mol% of catalyst, 3 equiv. dimethylmalonate, 3 equiv. BSA, 10 mol% CsOAc unless stated otherwise.
b: Determined by HPLC using Daicel Chiralcel ® OD column (Hexane/ ^{i}PrOH 99:1)
Absolute configuration by comparison with known Pd catalysed products. [80]
c: 10 mol % $Pt(dba)_2$ used. Reaction carried out in THF using preformed $NaCH(CO_2Me)_2$ as nucleophile.

When $Pt(dba)_2$ and (*S*)-P^N was used as the catalyst system, (Table 3.1: entries 3 & 4) a highly enantioselective reaction was realised, but only a trace amount of product was obtained. This catalytic system was tested again under many different conditions, but we never found a system that gave good turnover. It has recently been reported that palladium dba complexes are less active catalysts than the combination of palladium (II) and a reducing agent.[106] In order for allylic alkylation reactions to proceed the dba has to be replaced by the allylic acetate and studies on diphosphine platinum complexes, (P^P)Pt(dba) have revealed that dba is not displaced easily, even by phosphine ligands.[107]

We then spent some effort trying to prepare zerovalent platinum complexes of ligand **(64)**. Attempts to prepare Pt^0 compounds from $Pt(dba)_2$ and **(64)** gave unknown complex mixtures. If we tried to prepare $[(S)\text{-P^N}]_2Pt$, $[(S)\text{-P^N}]_3Pt$, or $[S)\text{-P^N}]_4Pt$ by the same method used for the preparation of $(Ph_3P)_4Pt$ (K_2PtCl_4, ligand, EtOH, KOH), we isolated a black insoluble material, assumed to be platinum metal. Hydrazine reduction of compound $[(S)\text{-P^N}]PtCl_2$ in the presence of (*S*)-P^N gave an air stable yellow powder which gave complex NMR spectra. Chemical analysis showed the compound contained far too much nitrogen, so it is suggested to be a hydrazine containing product. None of the complexes isolated showed catalytic properties.

After a few further studies, it became clear that we needed to find out what types of complexes would catalyse the reaction with maximum efficiency. To this end, the complexes in Table 3.2 were prepared and tested. The catalysts in entries 1-5, and 7 (in Table 3.2) were either prepared by a literature procedure or purchased. $[(dppe)PtC_3H_5]BF_4$ **(150)** was prepared as for $[(PPh_3)Pt(C_3H_5)]BF_4$ (Fig. 3.18).[108]



(150)

Fig. 3.18

Each of these compounds was tested under identical conditions in the standard reaction (Fig. 3.17) shown.

Table 3.2. Types of platinum complexes that catalyse allylic alkylation of acetate **(112)** at room temperature.[a]

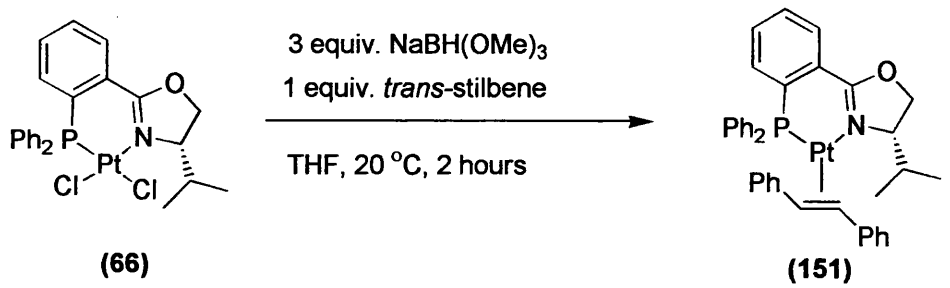
Entry	Catalyst	Conversion (T.L.C) (Isolated yield) [b]
1	$(Ph_3P)_4Pt$	100 (82)
2	$(Ph_3P)_2Pt$-ethylene	100 (88)
3	$(dppe)_2Pt$	0 (0)
4	$(Ph_3P)_2Pt$-trans-stilbene	100 (not isolated)
5	$[(PhO)_3P]_4Pt$	0 (0)
6	$[(dppe)PtC_3H_5]BF_4$	100 (78)
7	$(Ph_3P)_2PtCl_2$ and $NaBH(OMe)_3$	100 (85)

a: Conditions: 5 mol % Pt catalyst, 1.7 equiv. $NaCH(CO_2Me)_2$, 16 hrs at 20 °C in dry THF.
b: isolated yield after purification by column chromatography.

It appears that in the platinum catalysed reaction, the source of zerovalent platinum is crucial to the high reactivity of the system. The lower reactivity of zerovalent bis-diphosphine complexes (entry 3) is not observed in the palladium catalysed reaction, and it has been suggested that $(dppe)_2Pd$ is a more reactive catalyst than $(Ph_3P)_4Pd$. The complexes that do not act as catalysts at 20 °C are thought to be less prone to dissociation into a co-ordinatively unsaturated species. It is therefore plausible that the oxidative addition step of the reaction does not occur at room temperature for these compounds.

Having found out more about the type of procatalyst required, we returned to the enantioselective reaction. In order to avoid contamination from less enantioselective reaction pathways during the reactions, it seemed most appropriate to synthesise a procatalyst that contains a single phosphino-oxazoline ligand which chelates to the platinum. This should also fulfil the requirement of having a co-ordinatively unsaturated species undergoing the oxidative addition reaction.

As $(Ph_3P)_2Pt$-*trans*-stilbene was a convenient and active catalyst, we attempted to prepare the enantiomerically pure analogue [(*S*)-P^N]Pt-*trans*-stilbene, **(151)**. Enantiomerically pure platinum complexes of *trans*-stilbene are of considerable interest in their own right as models for enantioface recognition of alkenes.[109, 110] Complexes of this type are typically prepared by reduction of the corresponding dichloro complex, $LPtCl_2$ in the presence of the alkene. We had already prepared [(*S*)-P^N]$PtCl_2$, **(66)** (Chap.2, Fig. 2.7). Reduction of this compound in the presence of *trans*-stilbene was carried out using $NaBH(OMe)_3$ as reducing agent, and gave an orange-brown solid which is suggested to contain the desired product, **(151)**.



(66) **(151)**

Fig. 3.19 Attempted preparation of the zerovalent *trans*-stilbene complex (151)

However, the complex was impure, and all our attempts at recrystallisation resulted in decomposition. Importantly, the use of the impure complex **(151)** as allylic substitution catalyst gave a moderate yield of enantiomerically enriched product, **(149)**, providing that the reaction was carried out at reflux temperature (42% yield; 75% e.e.; 72hrs, 65 °C) It is noteworthy that complexes of the P,N bidentate ligand make less active catalysts than those derived from triphenylphosphine.

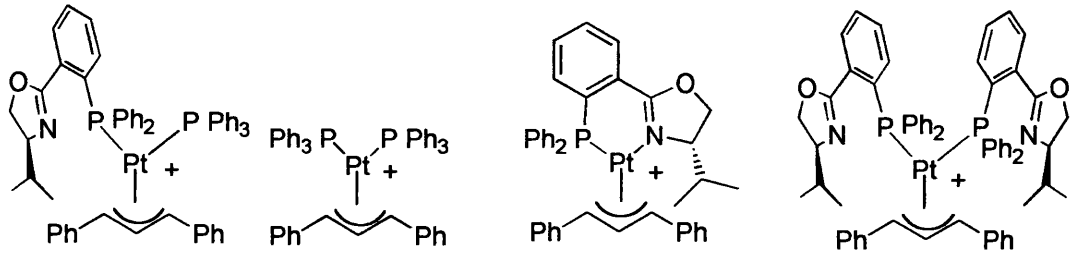
A combination of [(*S*)-P^N]$PtCl_2$ and $NaBH(OMe)_3$ was also tested as catalyst (Table 3.3). It was pleasing to observe good yields and enantioselectivity using this system at 65 °C (entries 3 and 4).

Table 3.3 Enantioselective allylic alkylation of acetate **(112)** using a combination of complex **(66)** and $NaBH(OMe)_3$ as catalyst.[a]

Entry	Additive	T / °C	t / h	Conversion[b] (isolated yield)	e.e. [b, c]
1	none	20	20	-	-
2 [d]	none	65	90	48	77 (S)
3	none	65	44	65 (-)	77 (S)
4	***5% ligand(1)***	***65***	***35***	***100 (93)***	***83 (S)***
5	10% ligand(1)	65	44	100 (-)	61 (S)
6	5% PPh_3	20	16	100 (91)	2 (S)
7	*trans*-stilbene	65	24	43 (-)	49 (S)
8 [e]	none	65	50	25 (-)	48 (S)

a: All reactions carried out in THF, using 1.7 equiv. $NaCH(CO_2Me)_2$ as nucleophile.
b: Determined by HPLC using Daicel Chiralcel ® OD column (Hexane/ ^{i}PrOH 99:1)
c: Absolute configuration by comparison with known Pd catalysed products. [80]
d: reaction carried out in acetonitrile
e: allylic acetate added prior to $NaBH(OMe)_3$

We suggest that [(*S*)-P^N]Pt ^{0}is the major species formed when complex **(66)** and $NaBH(OMe)_3$ are mixed together. Oxidative addition of the allylic acetate, **(112)** gives the desired platinum allyl complex containing one chelating phosphino-oxazoline ligand. Nucleophilic attack followed by dissociation of the product regenerates [(*S*)-P^N]Pt ^{0} which then starts the catalytic cycle off again. Whereas [(*S*)-P^N]$PtCl_2$ / $NaBH(OMe)_3$ requires 44 hours at 65 °C to obtain high conversion, [(*S*)-P^N]$PtCl_2$ / $NaBH(OMe)_3$ / PPh_3 gives a high yield (of racemic material) after 16 hours at 20 °C. The presence of triphenylphosphine, which might be expected to inhibit reaction by competing with the alkene for a co-ordination site, speeds up the reaction dramatically. In addition, running the reaction with 10 mol% of excess ligand reduces enantioselectivity considerably. All our results suggest that the fast, unselective allylic alkylations which are observed when triphenylphosphine is present in the reaction mixture (Table 3.1, entries 1 & 2; Table 3.3, entry 6) proceed predominantly through either complex **(152)** or **(153)** (Fig. 3.20). When excess phosphino-oxazoline ligand is present (Table 3.3, entry 5; Table 3.7, entry 4) the reaction probably proceeds *via* both complex **(154)** and complex **(155)**.



(152) **(153)** **(154)** **(155)**

Fig. 3.20 Competing pathways for platinum catalysed allylic alkylation when there is more than one ligand per Pt complex present

During the development of the above process, we found that the use of crude complex **(66)** as catalyst gives significantly lower enantioselectivity (50-60 % e.e.) than can be obtained under our optimum conditions. It is therefore important to take care in the purification of complex **(66)**. We also note here that the following catalysts systems either gave complex mixtures of products or no reaction at all. Complex **(66)** / NaOEt, complex **(66)** / NaOAc; complex **(66)** / DIBAL; K_2PtCl_4 / NaOAc / ligand **(64)**; $(COD)PtCl_2$ / ligand / Cp_2Co; complex **(66)** / AgOAc / ligand **(64)**

3.3 Comparison of catalytic performance with an isoelectronic palladium complex.

In order to make a strict comparison with the palladium catalysed reaction, the palladium complex, [(*S*)-P^N]$PdCl_2$, **(156)** was also prepared as shown in Fig. 3.21, and tested as a catalyst. If this catalyst is used with an excess of ligand, the enantiomeric excess actually goes up slightly, and is therefore a complete contrast to platinum (Table 3.4). If the palladium complex is reduced in the presence of triphenylphosphine, enantiomerically enriched products are still formed. The reactivity of the palladium catalyst is significantly reduced when it is used with excess ligand, which is also a complete contrast to platinum.

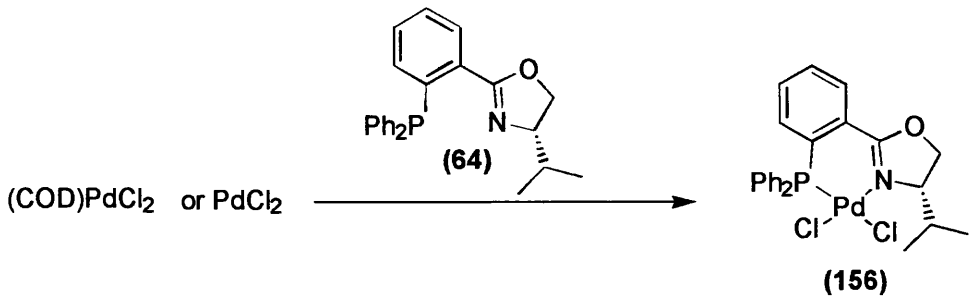


Fig. 3.21

Table 3.4 Enantioselective allylic alkylation of acetate **(112)** using a combination of palladium complex **(156)** and $NaBH(OMe)_3$ as catalyst.[a]

Entry	Additive	T / °C	t / h	Conversion[b]	e.e. [b, c]
1	none	20	20	100	91 (S)
2	5% ligand **(64)**	20	20	38	93 (S)
3	5% PPh_3	20	20	58	56 (S)

a: All reactions carried out in THF, using 1.7 eqv. $NaCH(CO_2Me)_2$ as nucleophile.
b: Determined by HPLC using Daicel Chiralcel ® OD column (Hexane/ ^{i}PrOH 99:1)
c: Absolute configuration by comparison with known Pd catalysed products. [80]

We have proposed that the more variable enantiomeric excess associated with our platinum catalysed reaction is due to the ligand being hemilabile when complexed to platinum. To support this, we added excess ligand to the complexes [(*S*)-P^N]$PtCl_2$, **(66)** and [(*S*)-P^N]$PdCl_2$, **(156)** and characterised the products formed by ^{31}P and ^{1}H NMR. In the case of platinum, compound **(66)** is instantly converted into complex **(67)** on addition of one equivalent of ligand (Fig. 3.22). This bis phosphino-oxazoline complex was previously observed as a by-product in the synthesis of complex **(66)** was characterised by NMR (chap.2, Fig. 2.7).

Even after extended reaction times, the palladium complex gives a mixture of free ligand, unchanged starting material, **(156)** and a new complex, which is presumably the palladium analogue of platinum complex **(67)**, as it shows one peak in the ^{31}P NMR spectrum. Hence, complexes **(66)** and **(156)** show different behaviour in the presence of excess ligand.

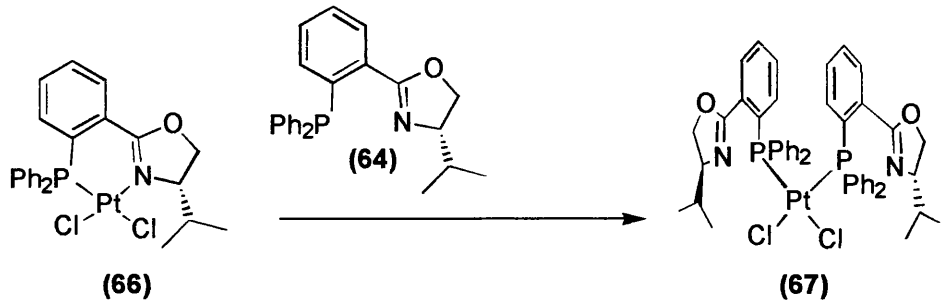


Fig. 3.22

Co-ordination chemistry of the type described here has potential to occur in any metal complex which contains heterobidentate ligands, and has considerable effects on the catalytic properties. Very recently, another group has observed similar chemistry for another set of heterobidentate ligands co-ordinated to palladium.[111] Measuring enantiomeric excess as a function of metal:ligand ratio should be an essential experiment in the testing of catalysts derived from chiral heterobidentate ligands.

3.4 Crystal structures of [(*S*)-P^N]$PtCl_2$, (66) and [(*S*)-P^N]$PdCl_2$, (156)

In order to fully establish the conformation of the two catalysts, the crystal structures of [(*S*)-P^N]$PtCl_2$, **(66)** and [(*S*)-P^N]$PdCl_2$, **(156)** were determined by

X-ray diffraction. ORTEX [60] views of the two structures are shown in figures 3.23 and 3.24 respectively. Selected geometric data is given in Tables 3.5 and 3.6 respectively. Further crystallographic data is provided in Appendix 1.

Both structures show that the ligand is bidentate and that it forms a six membered, puckered, chelate ring with the metal. All three carbon atoms in this ring reside above the plane of the complex with respect to the isopropyl group [C(23), C(22), C(24) for complex **(66)**].

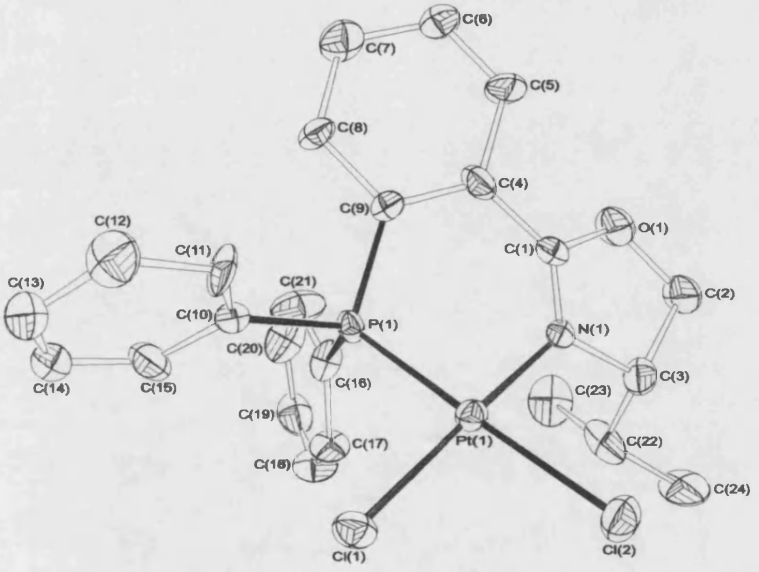


Fig. 3.23 Crystal structure of (*S*)-P^N)$PtCl_2$

Table 3.5. Bond lengths [Å] and angles [°] for [*(S)*-P^N]$PtCl_2$, **(66)**

Selected bond lengths[Å] for (66)		**Selected bond angles [°] for (66)**	
Pt(1)-N(1)	2.01(2)	N(1)-Pt(1)-P(1)	90.0(5)
Pt(1)-P(1)	2.192(5)	N(1)-Pt(1)-Cl(1)	176.1(5)
Pt(1)-Cl(1)	2.284(6)	P(1)-Pt(1)-Cl(1)	90.8(2)
Pt(1)-Cl(2)	2.363(6)	N(1)-Pt(1)-Cl(2)	90.2(5)
C(4)-N(1)	1.29(3)	P(1)-Pt(1)-Cl(2)	176.6(2)
		Cl(1)-Pt(1)-Cl(2)	89.2(2)

This conformation, common to other metal complexes of this ligand, forces the diphenylphosphino group to adopt an edge on/face on array. The overall shape and co-ordination environment surrounding the metal centres is similar within both crystal structures, despite the fact that the asymmetric unit in **(156)** incorporates one molecule of recrystallisation solvent (DCM). The metal-phosphorus bonds are c. 0.2 Å longer than the metal-nitrogen bond distances. The C=N bond which is 1.26Å in the crystal structure of the free ligand,[112] is 1.254(13) Å for the Pd complex and 1.29(3) Å for [(*S*)-P^N]$PtCl_2$. In both complexes the greater trans influence of the phosphine relative to the oxazoline is reflected in the significantly differing M-Cl bond lengths. The Pt-Cl bond *trans* to phosphorus is 2.363(6) Å, whereas the corresponding Pd-Cl bond is 2.379(3) Å. As such these metal-chlorine bond distances are, as expected, 0.1 Å longer than the M-Cl distances *trans* to the nitrogen atom.

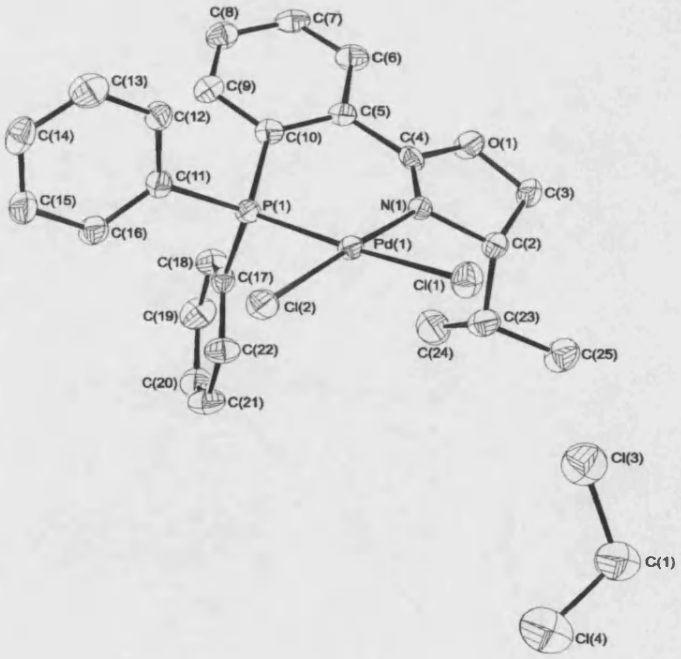


Fig. 3.24 Crystal structure of (*S*)-P^N)$PdCl_2$.DCM

Table 4.6. Bond lengths [Å] and angles [°] for [(*S*)-P^N]$PdCl_2$, **(156)**

Selected bond lengths[Å] for (156)		Selected bond angles [°] for (156)	
Pd(1)-N(1)	2.034(8)	N(1)-Pd(1)-P(1)	88.6(2)
Pd(1)-P(1)	2.217 (3)	N(1)-Pd(1)-Cl(2)	174.6(2)
Pd(1)-Cl(2)	2.294 (3)	P(1)-Pd(1)-Cl(2)	89.16(10)
Pd(1)-Cl(1)	2.379 (3)	N(1)-Pd(1)-Cl(1)	92.4(2)
C(4)-(1)N	1.254 (13)	P(1)-Pd(1)-Cl(1)	175.17(12)
		Cl(2)-Pd(1)-Cl(1)	90.26(10)

3.5 Enantioselective allylic alkylation using $[(C_3H_5)MCl]_n$ catalysts.

We also looked at the use of readily available $[(\eta^3\text{-}C_3H_5)PtCl]_4$ in the presence of (*S*)-P^N as a catalyst for this reaction (Table 3.7). The highest e.e. (90%) was observed at room temperature when conversion was low. When the reaction was carried out in THF at reflux, high conversion into product could be observed (74% yield: 84 % e.e.).

Table 3.7 Enantioselective allylic alkylation of acetate **(112)** using a combination of $[(C_3H_5)PtCl]_4$ and (*S*)-P^N as catalyst. [(a)]

Entry	Ligand (1) added (%)	T / °C	t / h	Conversion [(b)] (isolated yield)	e.e. [(b, c)]
1	5%	20	72	25 (-)	90 (S)
2	5%	65	48	81 (74)	84 (S)
3	10%	20	24	32 (-)	86 (S)
4	10%	65	44	100 (90)	57 (S)
5	5% [(d)]	65	48	- (37)	17 (S)

a: All reactions carried out in THF, using 1.7 equiv. $NaCH(CO_2Me)_2$ as nucleophile.
b: Determined by HPLC using Daicel Chiralcel ® OD column (Hexane/ ^{i}PrOH 99:1)
c: Absolute configuration by comparison with known Pd catalysed products. [80]
c: Prior to reaction, $AgBF_4$ is added to solution of $[(C_3H_5)PtCl]_4$ and **(1)**, (AgCl is filtered off)

When the metal to ligand ratio is 1 : 2, the enantiomer excess of the product formed drops to 57%. This is of course consistent with the explanation given in Fig. 3.20. The palladium catalysed reaction gives products of 97% e.e. under identical conditions (Pd : **(64)** = 1:2). If $AgBF_4$ is added to the mixture of $[(\eta^3\text{-}C_3H_5)PtCl]_4$ and (*S*)-P^N prior to the reaction the e.e. is diminished considerably. This effect has also been observed by other workers using palladium catalysts.[111]

The reactions discussed in tables 3.3 and 3.7 could be monitored by HPLC. The HPLC system that was set up allowed the detection of both enantiomers of product and starting material to be detected. Several samples that were taken prior to the consumption of all the starting material revealed that the enantioselectivity of the product is constant throughout the reaction, and that the e.e. of the starting material gradually increases as the reaction progresses and reaches 72% at 81% conversion. In other words one enantiomer of allylic acetate is being used up in preference to the other. This is also the case with the palladium / ligand **(64)** catalysts.

Using both the $[(S)\text{-P^N}]PtCl_2$ / $NaBH(OMe)_3$ and $[(\eta^3\text{-}C_3H_5)PtCl]_4$ / (*S*)-P^N catalyst systems, it is possible to obtain good enantioselectivity and good to excellent yields. The e.e.'s obtained are, however, slightly less than has been observed with palladium and ligand **(64)**. It is not clear whether this is due to a very small amount of the reaction going through pathway **(155)** (in Fig. 3.20) even under the optimised conditions, or due to the increased temperatures required to obtain high conversion.

In addition, some other difference between platinum and palladium may make 84-90 % e.e. the highest possible enantioselectivity for a platinum catalyst derived from ligand **(64)**.

3.6 Platinum catalysed allylic substitution using other nucleophiles and substrates

With the enantioselective allylic alkylation reaction using (*S*)-P^N as ligand quite well understood, we examined the scope of platinum catalysed allylic substitution with respect to the nucleophile and substrates. The nitrogen nucleophiles potassium phthalimide and benzylamine were tested. The reaction using potassium phthalimide with (Ph_3P)Pt-stilbene catalyst gave no product even after extended reaction times at 65 °C. The use of benzylamine as nucleophile, however, gave an excellent yield of known *rac*-(*E*)-N-benzyl-(1,3-diphenyl-2-propenyl)amine,[113] **(157)** after 16 hours at 20 °C (Fig. 3.25).

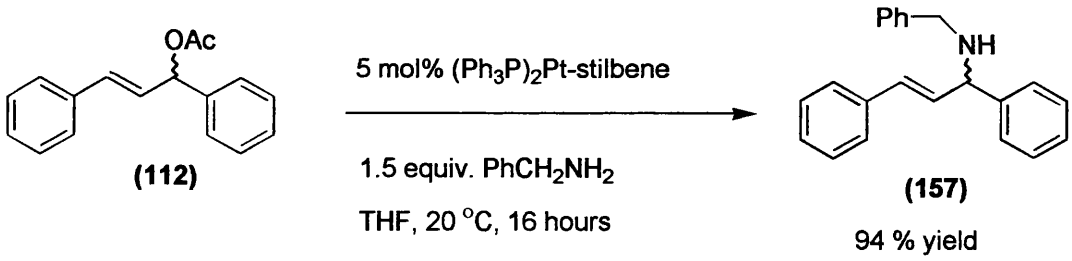


Fig. 3.25

Phenol could also be used as a nucleophile at room temperature when KF on alumina was used as base (Fig. 3.26).

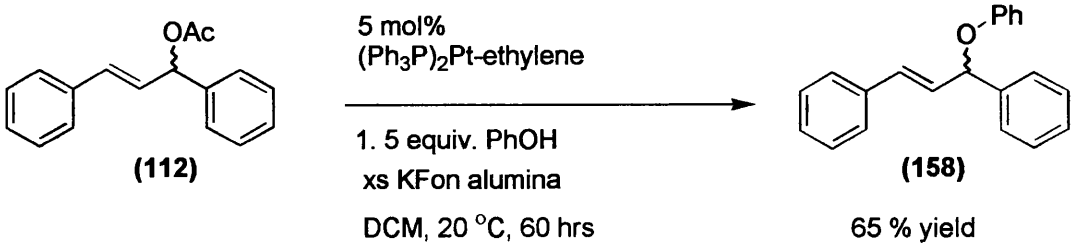


Fig. 3.26

A curious fact observed by one of my colleagues was that palladium catalysed nucleophilic substitutions using phenol as nucleophile and (*S*)-P^N as ligand always gave racemic products.[114] A possible explanation for this might be attack at the palladium centre first, followed by unselective elimination of product, or Pd catalysed racemisation of the products (phenol is quite a good leaving group). As platinum is both more oxophobic and less reactive than palladium, we tried the above platinum catalysed reaction in the presence of (*S*)-P^N. The products, however, were racemic.

The platinum catalysts can be used with a number of other substrates. These are mainly discussed in Chapter 4. Here we note that the cyclic substrate, cyclohexenyl acetate, **(159)** reacts with sodium dimethylmalonate at room temp. with no problems to give the desired product, **(160)**, (using either $(Ph_3P)_2Pt$-stilbene or $[(C_3H_5)PtCl]_4$ / dppe as catalyst), whereas the more hindered 1,1,3-triphenylprop-2-enyl acetate, **(161)** does not react with this nucleophile even after several days at 65 °C.

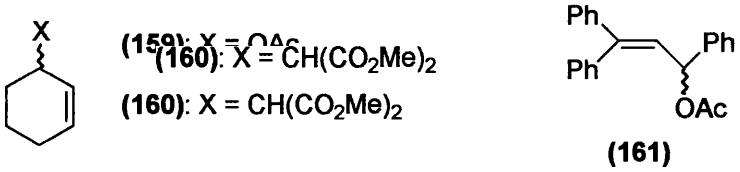


Fig. 3.27

3.7. Enantioselective allylic alkylation using (*S,S*)-chiraphos as ligand

As we had found the combination dppe, **(162)**/ $[(C_3H_5)PtCl]_4$ to be an active room temperature catalyst, we tested a combination of $[(C_3H_5)PtCl]_4$ and (*S,S*)-chiraphos, **(163)** as catalyst for the standard alkylation of 1,3-diphenyl prop-2-enyl acetate, **(112)** with sodium dimethylmalonate. The pioneering research of Bosnich and co-workers showed that, for this particular substrate, high yields (100 % conversion.) but only 22 % e.e. could be obtained when $[(chiraphos)Pd(C_3H_5)]^+ ClO_4^-$, **(165)** was used as catalyst for this reaction.[115]

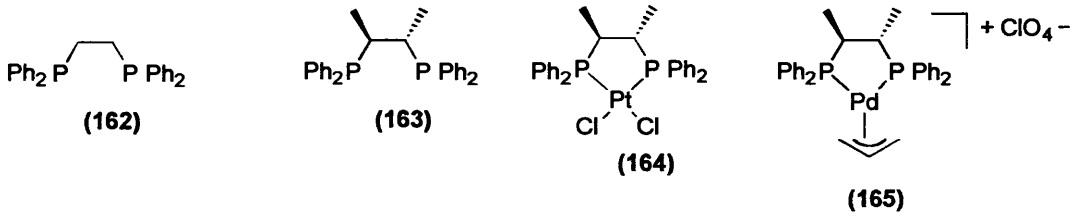


Fig. 3.28

We felt pretty confident that $[(C_3H_5)PtCl]_4$ / (*S,S*)-chiraphos would be an active room temperature catalyst that would probably only give low to moderate e.e. The results obtained were surprising (Table 3.8)

The reactions were slow at 20 °C and gave moderate conversion but with 95% e.e. After several attempts at carrying out the reaction at higher temperature, we still only observed fairly moderate conversion (in addition, e.e.'s were somewhat lower at 50-65°C). We also prepared complex **(164)** by the literature procedure,[116] and used it as a catalyst in combination with $NaBH(OMe)_3$ reducing agent. No products were observed at room temperature, while at reflux, conversion was still low (32 % conversion: 69 % e.e.).

Table 3.8 Enantioselective allylic alkylation of acetate **(112)** in the presence of (*S,S*)-chiraphos [a]

Entry	Catalyst	Temp. (°C)	Time (hrs)	Conversion [b]	e.e. [b, c]
1	5% $[(C_3H_5)PtCl]_4$	20	72	39	95 (S)
2	5% $[(C_3H_5)PtCl]_4$	56	67	57	74 (S)
3	5% (54) / 10% $NaBH(OMe)_3$	65	60	32	69 (S)
4	5% $[(C_3H_5)PdCl]_2$	20	16	100	85 (S)

a: All reactions carried out in THF, using 1.7 equiv. $NaCH(CO_2Me)_2$ as nucleophile

b: Determined by HPLC using Daicel Chiralcel ® OD column (Hexane/ ^{i}PrOH 99:1)

c: Absolute configuration by comparison with known Pd catalysed products. [80]

Comparing the structures of dppe and chiraphos, it is surprising that the platinum complexes formed from these ligands showed considerably different catalytic activity. As the excellent e.e. observed with platinum was in contrast to the palladium catalyst, **(165)**, $[(C_3H_5)PdCl]_2$ / (*S,S*)-chiraphos was checked as a catalyst in the same reaction. Complete conversion into product with 85 % e.e. was observed. We later found a separate report describing similar e.e. using $[(C_3H_5)PdCl]_2$ / (*S,S*)-chiraphos as catalyst.[117] It is not clear what causes the difference between the Bosnich and co-workers low e.e.'s using **(165)** as catalyst and the two subsequent reports. On one hand, analytical error could be responsible. However, the systems that gave good e.e. both contain chloride ions. Halide ions have been known to have an effect on the outcome of allylic alkylation reactions,[118] but this would be a most dramatic example if a halide effect were at work here. To date, we have not investigated these intriguing differences further. It may also be of note that the platinum catalyst gave higher e.e. than palladium.

In summary, we have developed a highly enantioselective platinum catalysed allylic alkylation reaction. Considerable experimentation eventually revealed that either [(*S*)-P^N]$PtCl_2$ / $NaBH(OMe)_3$ or $[(C_3H_5)PtCl]_4$ / (*S*)-P^N catalyst systems would give high e.e., providing the ligand:metal ratio is not greater than one. Our catalytic experiments, along with an NMR study, have showed that ligand **(64)** is hemilabile when complexed to platinum (but not palladium). The catalysts derived from ligand **(64)** are considerably less active than those derived from triphenylphosphine. This is also a contrast to the palladium catalysed reaction. The crystal structures of the isoelectronic complexes [(*S*)-P^N]MCl_2 were obtained. These suggest that there are no marked differences in the conformation of the ligand when bound to the different metals. The platinum catalysed reaction was also extended to an "N" and an "O" nucleophile.

When using (*S,S*)-chiraphos as the ligand, excellent e.e.'s were observed, which was surprising in light of previous studies using palladium catalysts. Several intriguing differences in the co-ordination chemistry of platinum and palladium can be inferred from the experiments described in this chapter. In order to study and exploit the properties of platinum catalysts further, we next turned our attention to the issues of obtaining regioselectivity in metal catalysed allylic alkylation (Chapter 4).

Chapter 4.

Regioselectivity of Nucleophilic Attack in Platinum and Palladium Catalysed Allylic Alkylation

An issue which must be addressed in an allylic alkylation reaction is regioselectivity. As the reaction proceeds through an η^3- allyl complex, the nucleophile can potentially attack at any of the three allylic carbon atoms. In general, palladium catalysts show a preference for attack at one of the terminal allylic carbon atoms, and if there is a choice between attack at a primary, secondary or tertiary carbon, the nucleophile generally adds to the less substituted carbon atom. Attack at the middle carbon of a palladium allyl complex is sometimes observed particularly when a less stabilised nucleophile is used. We wished to find out more about the regioselectivity of nucleophilic attack in platinum catalysed allylic alkylation.

4.1 Nucleophilic attack at the central carbon atom

Less stabilised nucleophiles have been shown to attack at the central carbon of a π-allyl palladium complex and then to reductively eliminate cyclopropanes.[119, 120]

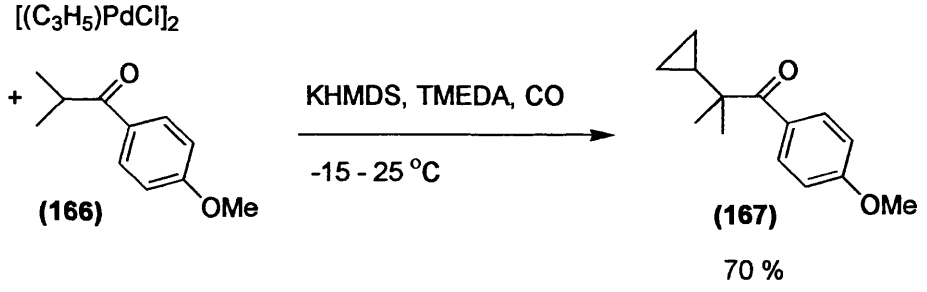


Fig. 4.1

This reaction has attracted considerable attention from both an experimental and theoretical standpoint. Theoretical calculations initially predicted the process to be energetically unfavourable.[121] Recent studies have lent insight into what factors cause nucleophilic attack on central (rather than terminal) carbon atoms.[122, 123]

When ketene silyl acetals react with palladium allyl complexes, a mixture of allylic alkylation and cyclopropane products results (Fig. 4.2).[122, 124]

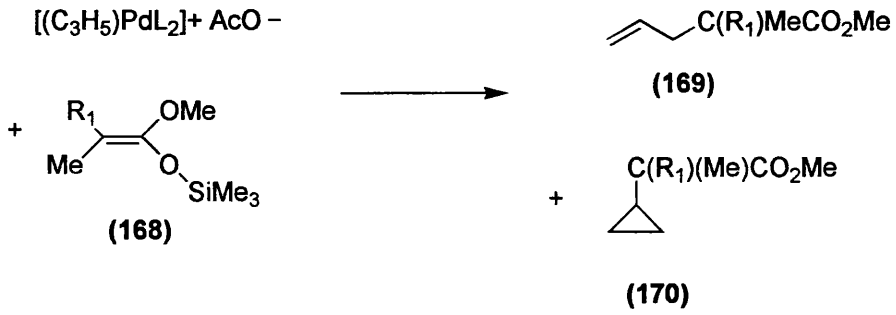


Fig. 4.2

Interestingly, adding ketene silyl acetals to platinum allyl complexes proceeds with excellent regioselectivity, and stable platinacyclobutane complexes **(171)** can be isolated (Fig. 4.3).[122, 125]

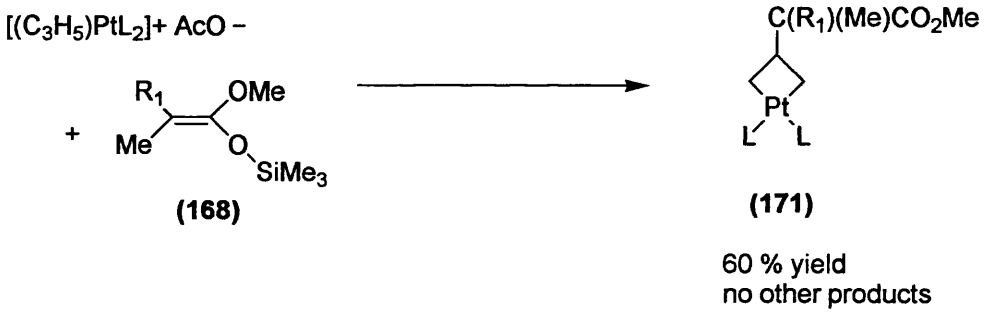


Fig. 4.3

Studies on the η^3-2-chloro-propenyl palladium complex, **(172)** provides the first example of a highly stabilised nucleophile attacking at the central carbon atom.[123] A remarkable ligand effect was observed: If a palladium allyl complex of TMEDA or bipy was reacted with methyl diethyl malonate, complete selectivity towards compound **(174)** was observed. This compound arises from nucleophilic attack at the central carbon atom, followed by elimination of chloride to regenerate an allyl complex followed by attack at the terminal allylic carbon to give product. If

palladium complexes of phosphine, alkene, or sulfur ligand were used, the terminal carbon atom was attacked and product **(175)** was generated.

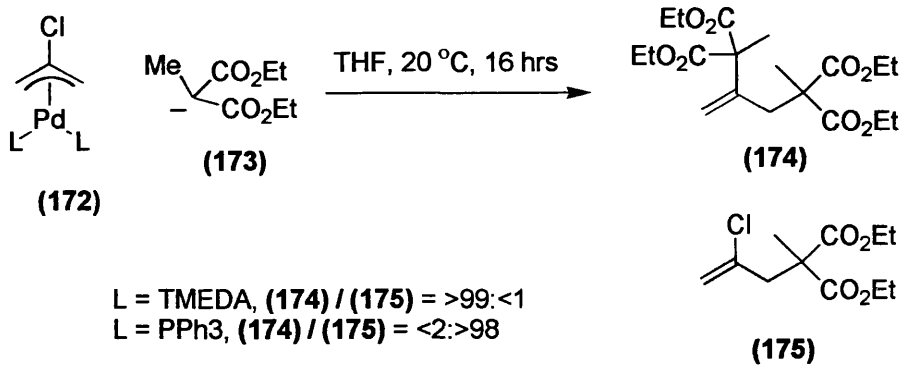


Fig. 4.4

Theoretical calculations predicted that for a Frontier Molecular Orbital (FMO) controlled nucleophilic attack, TMEDA complexes favour central attack, whereas phosphine complexes give terminal attack. In particular, the two lowest unoccupied molecular orbitals swap in energy when the ligand is changed from TMEDA to PH_3. It is thought that the energies of these orbitals determine the regioselectivity of attack. If the reaction has a charge control component, phosphine ligands predict a terminal attack. For TMEDA complexes the positive charge on the allyl ligand will be significantly less, and the reaction is more likely to be under FMO control. The theoretical calculations also predict that a less stabilised nucleophile will show a greater tendency for central attack. This also fits in with the experimental data.[122, 123]

It has recently been shown that $(Ph_3P)_4Pd$ catalyses a double substitution of substrate **(176)**, providing phenol derivatives are used as nucleophiles (Fig. 4.5).[126]

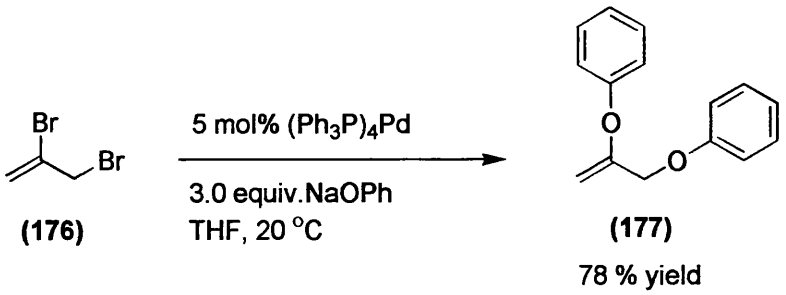


Fig. 4.5

The study which most caught my eye was reported in 1994.[99] Ten mol% of $(Ph_3P)_2Pt$-ethylene *catalyses* the reaction of 2-chloroallyl acetate, **(178)** with stabilised nucleophile, methyl diethylmalonate to form product **(174)**. If $(Ph_3P)_4Pd$ was used as catalyst, the standard allylic alkylation product, **(175)** was observed (Fig. 4.6). Compound **(175)** is not converted into the doubly alkylated product, **(174)** under the reaction conditions, which suggests that central attack of the nucleophile is the initial step in the reaction.

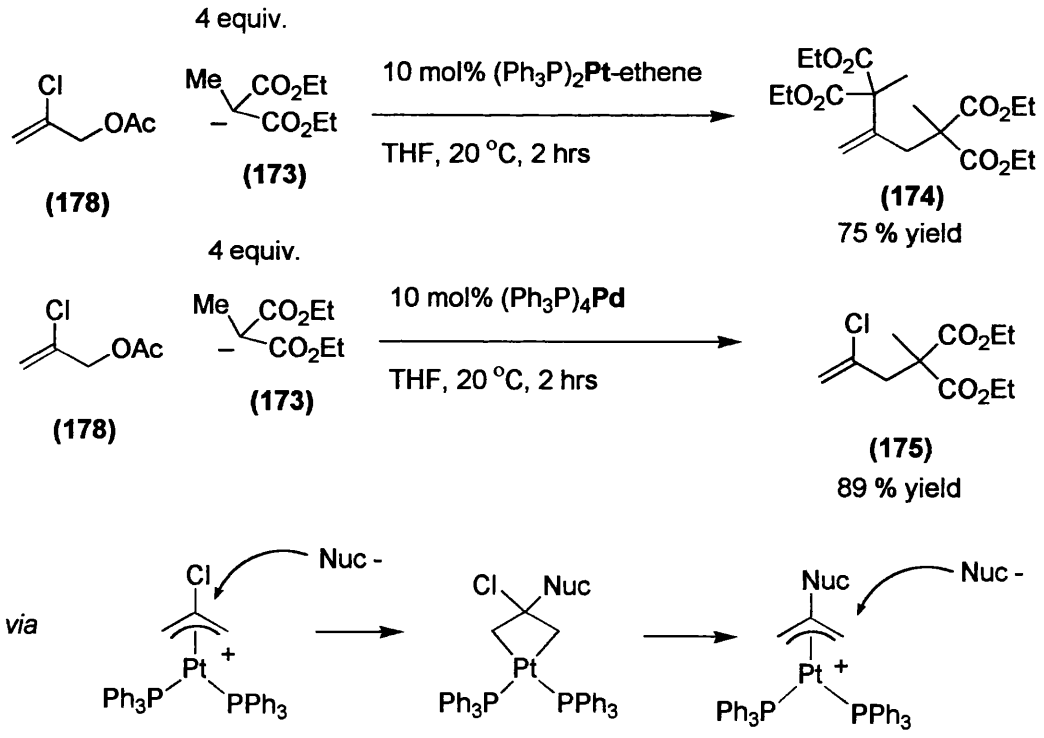
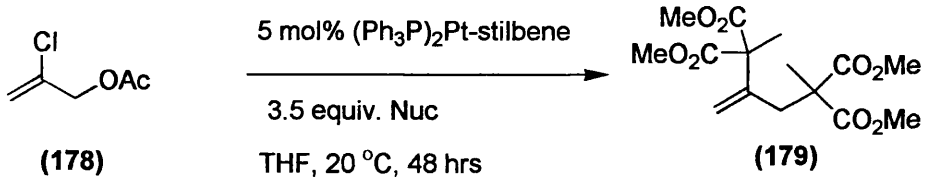


Fig. 4.6

We felt that this reaction merited further study, as it is mechanistically interesting and because it might be of considerable potential for organic synthesis. As a starting point, we performed similar experiments to those of Murai *et. al.* 2-chloro allyl acetate was reacted with 3.5 equivalents of methyl dimethylmalonate in the presence of 5 mol% $(Ph_3P)_2Pt$-stilbene at 20 °C (Fig. 4.7). It was pleasing to observe the desired double alkylation product, **(179)** which arises from initial central attack on the allyl platinum species. We could not isolate the desired product when we used either benzylamine or dimethyl malonate as nucleophile.



Nuc = $NaC(Me)(CO_2Me)_2$: 63 %

Nuc = $NaCH(CO_2Me)_2$: 0 %
Nuc = H_2NBn : 0%

Fig. 4.7

To investigate if a vinyl iodide would undergo a similar reaction, we prepared and tested compound **(182)**. Formation of the known acetate, **(182)** by iodination, reduction and acetylation was straightforward and had previously been described (Fig. 4.8).[127, 128]

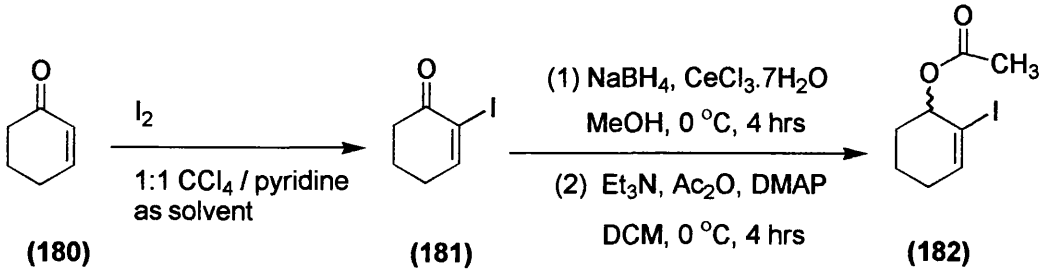
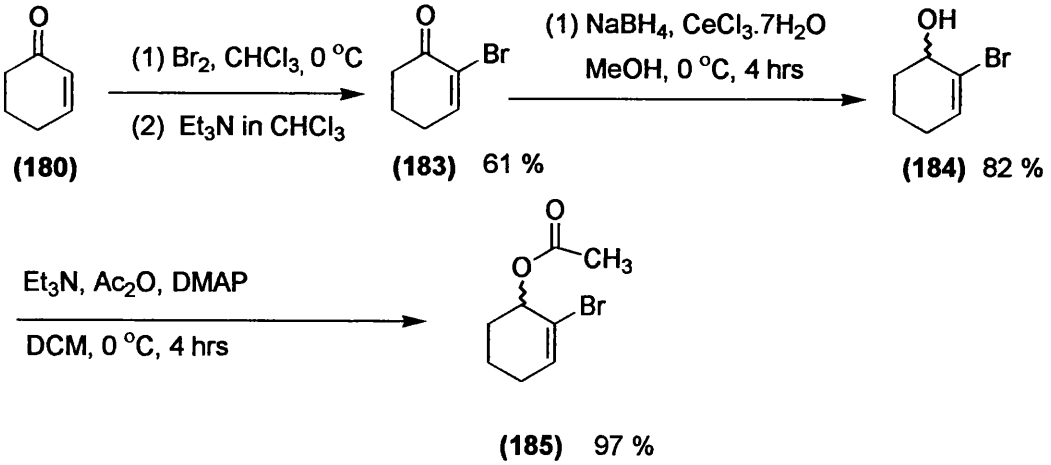


Fig. 4.8

Unfortunately, compound **(182)** is unreactive in allylic alkylation reactions using methyl dimethylmalonate and no double or single substitution products were formed (Fig. 4.10). A possible reason for the failure of the reactions was the vinyl iodide functionality oxidatively adding to the zerovalent platinum species before the allylic acetate could. This would generate an unreactive vinyl-platinum complex. Another explanation is that relatively low (w.r.t. chloride) electronegativity of iodide did not activate the central carbon to attack by the nucleophile (although we might expect to see conventional terminal substitution products in this case). Whatever was going wrong, it seemed worth trying out some vinyl bromides in the reaction, as the central carbon should be more activated to nucleophilic attack, and less likely to form unreactive vinyl-platinum species than iodide, **(182)**. Bromination of cyclohexenone[129] was straightforward and gave a good yield of ketone **(183)**. Luche reduction, followed by acetylation gave the desired acetate **(185)** (Fig. 4.9).



(180) **(183)** 61 % **(184)** 82 %

(185) 97 %

Fig. 4.9

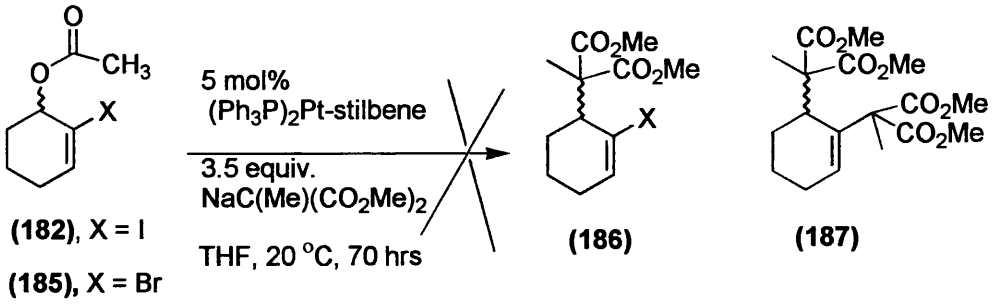


Fig. 4.10

Frustratingly, this compound was also unreactive in platinum catalysed allylic alkylation (Fig. 4.10). In fact, the only product isolated was alcohol **(184)**. As a last attempt, we prepared acetate **(190)** by addition of phenyl magnesium bromide to α-bromo-cinnamaldehyde, followed by acetylation of the alcohol, **(189)**. Yet again, no double substitution products were observed when acetate **(190)** was subjected to our standard alkylation procedure (Fig. 4.11). Alcohol **(189)** was isolated.

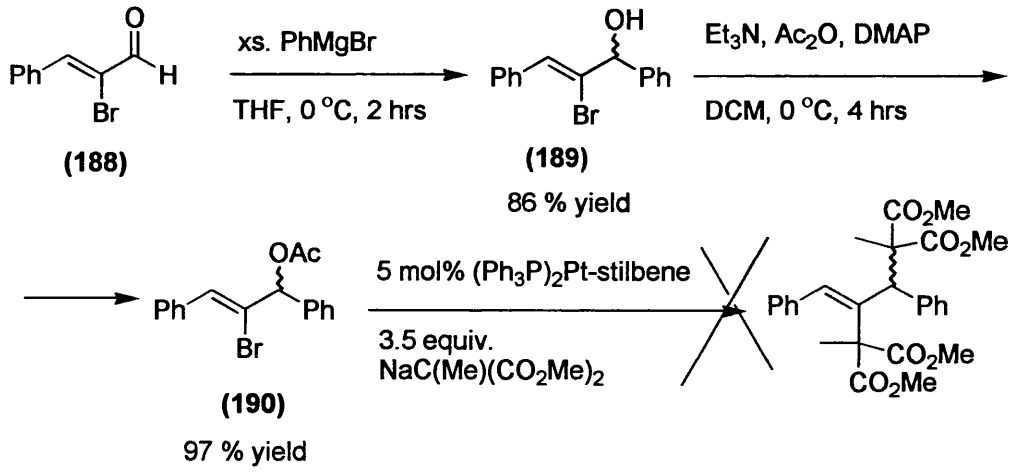
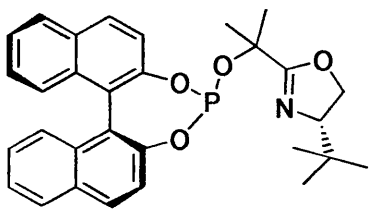


Fig. 4.11

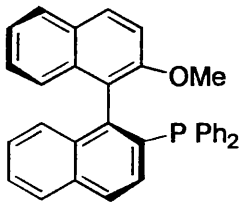
My time in the lab was by now coming to an end, and we abandoned this work at this point. In conclusion, we attempted to develop a platinum catalysed double substitution reaction. Our results suggest the process is very limited in terms of nucleophile and substrate.

4.2 Controlling regioselectivity of nucleophilic attack on an unsymmetrical allyl complex

A more common and equally challenging regiochemical problem is how to control the site of attack when the reaction proceeds through an unsymmetrical intermediate. When a mono-substituted allylic acetate is used as substrate, palladium catalysts normally give a mixture of isomers with a strong tendency to form the linear product. A few ligands, however, have recently been shown to reverse this regioselectivity. For example, when cinnamyl acetate is alkylated using sodium dimethylmalonate, most ligands give mainly linear products. Pfaltz and co-workers developed ligand **(191)** which can reverse this bias.[130] The "MOP" ligand, **(192)** has also been shown to reverse the regiochemistry of these reactions.[131] Other studies have shown that most readily available ligands give predominantly linear products in palladium catalysed allylic alkylation reactions.



(191)

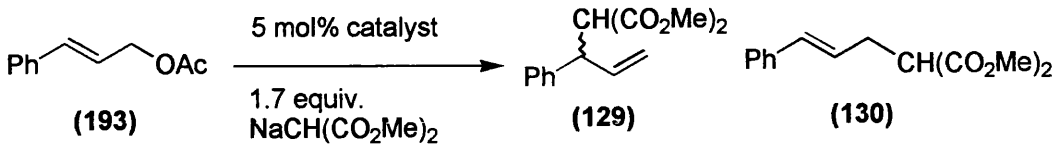


(192)

Fig. 4.12

Recently, the most promising studies have used other metals as catalysts. As discussed in Chapter 3, Ir, Rh, Ru, and Mo catalysts can all give predominantly branched products under the right conditions. As both Brown and Kurosawa had used platinum catalysts to alkylate butenyl acetate with better regioselectivity than with palladium, we elected to study regioselectivity in platinum catalysed allylic substitutions which proceed through unsymmetrical intermediates.

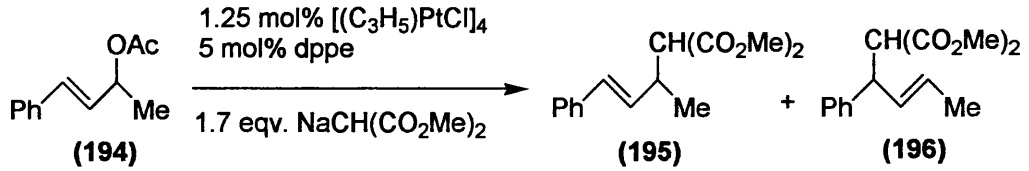
Using 5 mol% $(Ph_3P)_2Pt$-stilbene as catalyst, and cinnamyl acetate, **(193)** as substrate, a high yield of the two regioisomers, **(129)** and **(130)** was obtained. The branched: linear ratio is similar to a related palladium catalyst (Fig. 4.13).



$(Ph_3P)_2Pt$-stilbene cat.: **(129) / (130)** = 18 : 82
$[(C_3H_5)Pd(PPh_3)_2]Cl$ cat.: **(129) / (130)** = 13 : 87

Fig. 4.13

The unsymmetrically substituted acetate, **(194)** can give compounds **(195)** and **(196)** as products. There is generally a good preference for compound **(195)**, probably because this product has a more electron withdrawing double bond which can stabilise the intermediate palladium (0) olefin complex. It has been found that when acetate **(194)** is alkylated using $[(C_3H_5)PdCl]_2$ / dppe, the two regioisomers, **(195)** and **(196)** are formed in a ratio of 10.5:1.[132] When sparteine is used as ligand, the regioisomers form in a ratio of 4.8 :1.[133] We obtained slightly improved selectivity when a combination of $[(C_3H_5)PtCl]_4$ and dppe was used a catalyst, [**(195) / (196)** = 15:1] (Fig. 4.14).



$[(C_3H_5)PtCl]_4$ / dppe: **(195) / (196)** = 15:1
combined yield = 92 %

Fig. 4.14

We tested the platinum catalysts in the alkylation of but-2-enyl acetate, **(125)** (Fig. 4.15). The results are shown in Table 4.1. When the platinum catalysts contain either PPh_3 or (*S*)-P^N as ligand, regioselectivity was poor, although there is a greater proportion of branched products when compared to palladium.

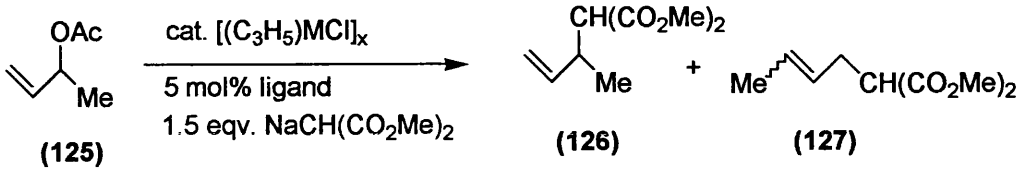


Fig. 4.15

Of particular interest is entry (5): The use of bulky, electron rich tricyclohexylphosphine as ligand gives almost exclusive formation of branched products (**(126)** / **(127)** = 15:1) Surprisingly, the palladium catalysed reaction also gives excellent regioselectivity when this ligand is used (entry 6).

Table 4.1 Regioselectivity in the alkylation of but-2-enyl acetate, **(125)** using a variety of platinum and palladium catalysts

Entry	Catalyst [a]	(19)/(20) [b]
1	$(Ph_3P)_2Pt$-stilbene	2.1 : 1
2	$[Pd(\eta^3C_4H_7)Cl(PPh_3)_2]$ [c]	1 : 2.0
3	[(*S*)-P^N] / $[(C_3H_5)PtCl]_4$	1.0 : 1
4	[(*S*)-P^N] / $[(C_3H_5)PdCl]_2$	1 : 1.9
5	Cy_3P / $[(C_3H_5)PtCl]_4$	15 : 1
6	Cy_3P / $[(C_3H_5)PdCl]_2$	11 : 1

a: Reactions were run at 20 °C in THF using 1.5 equiv. $NaCH(CO_2Me)_2$ as nucleophile except entry 3 (THF, 65°C). In all cases conversion was 100 %. The *E/Z* ratio was not accurately determined, but in all cases the linear products were almost predominantly of *E* configuration.

b: determined by G.C. and confirmed by ^1H NMR

c: Reference 97

The same trends were observed when using hexenyl acetate, **(197)** (Fig. 4.16 & Table 4.2). However, in this case, there was a greater tendency for linear products to form. Only the platinum / tricyclohexylphosphine catalyst gives really good regioselectivity (c. 10:1) towards branched product, **(198)**. The use of (*S*)-P^N as ligand gives excellent regioselectivity towards the linear product.

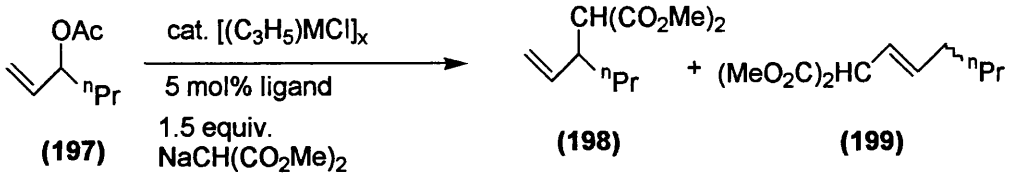


Fig. 4.16

Table 4.2 Regioselectivity in the alkylation of hex-2-enyl acetate, **(197)** using platinum and palladium catalysts

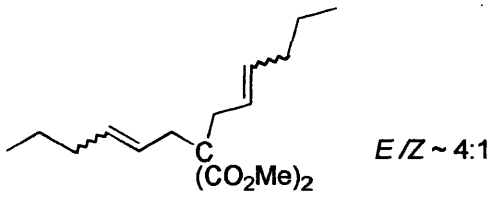
Entry	Catalyst [a]	(198)/(199) [b]	E / Z for (199)[b]
1	$(Ph_3P)_2Pt$-stilbene	1:1.8	10:1
2	Ph_3P / $[(C_3H_5)PdCl]_2$	1:4.1	10:1
3	[(*S*)-P^N] / $[(C_3H_5)PtCl]_4$	1:7.2	6:1
4	[(*S*)-P^N] / $[(C_3H_5)PdCl]_2$	1: 13.1	9:1
5	Cy_3P / $[(C_3H_5)PtCl]_4$	9.8:1	10:1
6	Cy_3P / $[(C_3H_5)PdCl]_2$	3.1:1	6:1

a: Reactions were run in THF at 20°C using 1.5 equiv. of $NaCH(CO_2Me)_2$ as nucleophile (except entry 3: THF, 65°C). In all cases conversion was 100 %.

b: determined by G.C. and confirmed by ^1H NMR

On some occasions, a small by-product could be detected by T.L.C. We isolated a small amount of this product and characterised it as diallylated product **(200)** by ^1H NMR and mass spectroscopy (Fig 4.17).

The ^{1}H NMR suggests there are at least two isomers present, as there are two almost identical signals for several of the proton resonances.



(200)

Fig. 4.17 Small amounts of diallylated product, (200) were sometimes observed

Kurosawa proposed that platinum catalysts give more branched product than palladium as a result of increased stability of the initial zerovalent platinum alkene product (platinum is a stronger π-donor than palladium). The branched products contain a more electron poor double bond, and are therefore favoured for platinum. Our results fit in with this hypothesis.

4.3 The use of tricyclohexylphosphine to obtain regioselectivity on palladium catalysed allylic alkylation

The results obtained using tricyclohexylphosphine as ligand are surprising. As good regioselectivity was observed with both platinum and (the normally preferred) palladium catalysts, it seemed important to study the ligand effect further, with respect to both its origin, and its synthetic potential. It is possible that the regioselectivity observed is a direct result of the basicity or bulkiness of a ligand. If this were the case, then other ligands would show this effect. Another possibility is that the specific shape of Cy_3P is such that only one ligand binds onto the palladium, with the other co-ordination site being taken up by chloride or acetate. An explanation similar to this has been suggested as the origin of the unusual

regioselectivity observed with the "MOP" ligand, **(192)**. To investigate if the regioselectivity was a general property of bulky, basic ligands, regiochemistry in the palladium catalysed alkylation of but-2-enyl acetate, **(125)** with sodium dimethylmalonate (Fig. 4.15) with a variety of ligands was studied. (selected results are shown in Table 4.3).

Table 4.3. Effect of ligand on the regioselectivity of allylic alkylation of **(125)**

Ligand [a]	**(126)/(127)** [b]	E / Z for **(127)** [c]
Tricyclohexylphosphine, Cy_3P	11.5:1	not detectable
Tricyclohexylphosphine Cy_3P $[(C_3H_5)PtCl]_4$ catalyst	15.4:1	not detectable
Ph_3P [d]	1:2.0	N / A
Ph_3P $(Ph_3P)_2Pt$-stilbene as catalyst	2.1:1	4.6:1
tris(2,4,6-trimethoxyphenyl)phosphine, $[(CH_3O)_3C_6H_2]_3P$	1:3.9	5.5:1
tri-*o*-tolylphosphine, $(CH_3C_6H_4)_3P$	1:1.5	5.5:1
methyldiphenyl phosphine	1:1.3	4.7:1
tri-(4-methoxyphenyl)phosphine, $(CH_3OC_6H_4)_3P$	1:1.2	5.7:1
tri-(4-fluorophenyl)phosphine, $(FC_6H_4)_3P$	1:1.3	5.1:1
tri-2-furylphosphine	1:2.2	6.4:1
1,2-bis(dicyclohexylphosphino)ethane, $Cy_2PCH_2CH_2PCy_2$	1:1.1	4.7:1
1,4-bis(diphenylphosphino)butane (dppb)	1:1.1	4.5:1
1,2-bis(diphenylphosphino)ethane (dppe)	1:1.4	6.4:1

a: all reactions run using 2.5 mol% $[(C_3H_5)PdCl]_2$ catalyst, 1.5 equiv. $NaCH(CO_2Me)_2$ nucleophile, THF solvent at 20 °C unless stated. In all cases conversion was 100 % as determined by G.C.

b: determined by G.C. and checked by ^1H NMR

c: determined by G.C.

d: taken from reference 97

Tricyclohexylphosphine is a bulky and strongly electron donating phosphine. This is quantified by its large cone angle (θ =170°)[134] and the large pKa value of its conjugate acid (pKa = 9.70). This can be compared with PPh_3 (θ = 145 °, pKa = 2.73).[135] The ligands in Table 4.3 were chosen as they share some characteristics with Cy_3P, and can therefore be used to ascertain whether the regioselectivity observed is a property of a general class of ligands. Tris-(2,4,6-trimethoxyphenyl)phosphine [136] is both more bulky and basic (θ = 184°, pKa = 11.02) than Cy_3P, but gives opposite regioselectivity to the Cy_3P / Pd catalysed reactions. Tri-*o*-tolylphosphine is one of the most bulky phosphines (θ = 194°, pKa = 3.08) and also gives predominantly linear products, again in contrast to the tricyclohexylphosphine system. Tris-(4-methoxyphenyl) and tris-(4-fluorophenyl) phosphines are informative as they have a similar cone angle (θ =145°) but different basicities (pKa's = 4.57 and 1.97 respectively).[135] It can be concluded that there is no direct trend between basicity or cone angle and the proportion of branched products observed for this particular reaction. The formation of predominantly linear products with a wide range of ligands has been observed for other substrates by other workers.[137]

To see if only one ligand was binding the palladium during reaction, a simple NMR experiment was carried out. Adding Cy_3P to $[(C_3H_5)PdCl]_2$ (ligand to metal : 2:1) generated a mixture of two complexes. ^{31}P NMR revealed that there is no free Cy_3P remaining in the solution. This suggested that the allyl intermediates do contain two Cy_3P ligands. Further evidence comes from the literature reports of the compounds $[(PCy_3)_2Pt(C_3H_5)]X$ (X = -OAc, $-BF_4$)[124] and $[(PCy_3)_2Pd(C_3H_5)]BF_4$.[138]

It is also known that the presence of chloride can have a significant effect on regioselectivity of allylic alkylation.[118] To investigate the effect of chloride on the Pd / PCy_3 catalysed reactions, $[(PCy_3)_2Pd(C_3H_5)]BF_4$, **(201)** was prepared by the literature route,[138] and tested as a catalyst for allylic alkylation of but-2-enyl acetate with sodium dimethylmalonate. The regioselectivity in this reaction was very similar to that found using the chloride containing catalyst $[(C_3H_5)PdCl]_2$ / PCy_3 (Fig. 4.18). The reaction outcome is therfore not significantly affected by chloride ions.

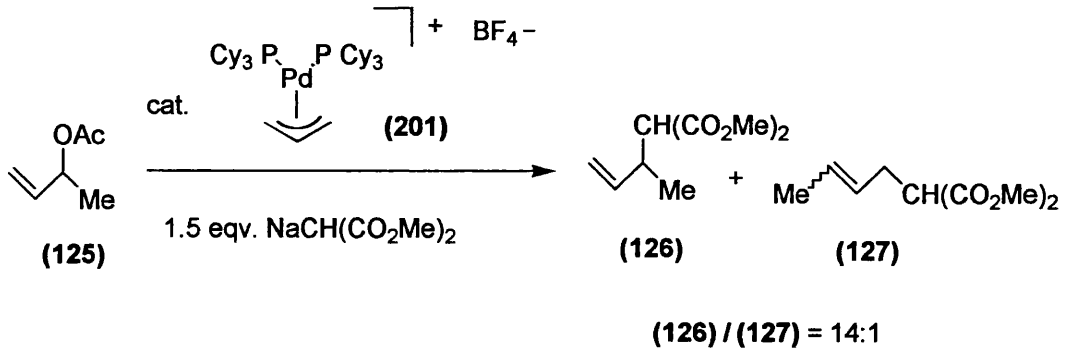


Fig. 4.18 Using the halide free palladium catalyst (200) gives similar regioselectivity to $[(C_3H_5)PdCl]_2$ / PCy_3 catalyst

It appeared at this stage that the unusual selectivity towards products containing a terminal double bond is not a result of the strong π-donor capacity of the $(Cy_3P)_2M$ fragments. It was suggested to us that the results obtained may be due to a strong "memory effect" [139] when Cy_3P was used as ligand (ie. the product is the same regioisomer as the starting material). To test this theory, the regioisomeric allylic acetates **(202)** and **(203)** were tested (Fig. 4.19).

The regioselectivity was altered (from 11.5:1 to 1.3:1 for **(202)** and from 3.1:1 to 1:8.8 for **(203)**), and much greater proportions of linear products (from linear starting material) was observed. This is good evidence that a partial memory effect is associated with this ligand.

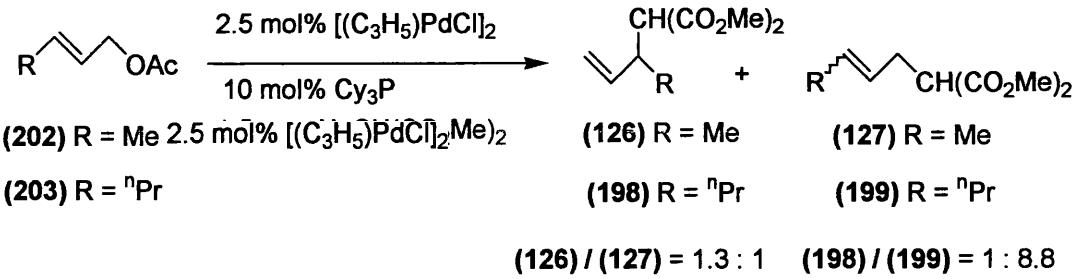
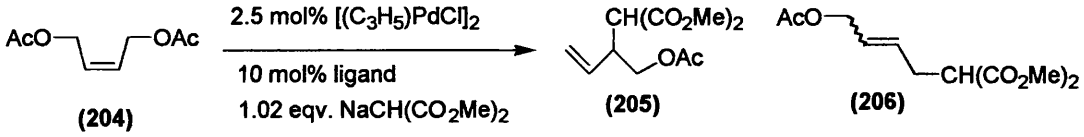


Fig. 4.19 Use of tricyclohexylphosphine-palladium catalyst gives different regioselectivity if linear allylic acetates are employed as substrates

We have also looked at the use of tricyclohexylphosphine-palladium catalysts in the allylic alkylation of commercially available *cis*-1,4-diacetoxy-2-butene, **(204)**. Allylic substitution on derivatives of diacetate **(204)** have previously yielded linear isomers.[140] Compound **(204)** has also been utilised in palladium catalysed heterocycle synthesis.[141] When compound **(204)** was alkylated with 1.02 equivalents of sodium dimethylmalonate using triphenylphosphine as ligand, predominantly linear products were observed (in addition to small amounts of by-products).

Switching ligand to Cy_3P gave a dramatic reversal of regiochemistry (B / L = 3.4:1) Pure branched isomer was isolated by column chromatography, albeit in only 39 % yield, due to the similar R_F of branched and linear products. This result does not fit in with the memory effect explanation as the starting material was linear.



Ligand	(205) / (206)	*E* / *Z* for(206)
PPh_3	8 / 92	1.8 : 1
PCy_3	77 : 23	2.2:1

Fig. 4.20

We also re-examined allylic alkylation of acetate **(194).** We were pleased to discover that when Cy_3P / $[(C_3H_5)PdCl]_2$ is used as catalyst, acetate **(194)** can be alkylated with complete retention of regiochemistry (Fig. 4.21). [**(196)** was not detected in the crude reaction product.]

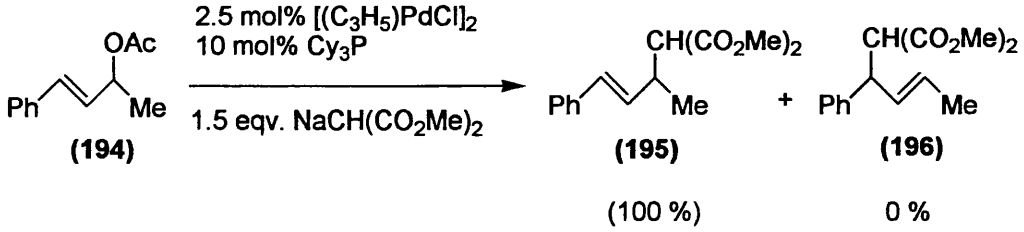


Fig. 4.21

Most of the results we have obtained using tricyclohexylphosphine - palladium catalysts suggest that the intermediate allyl complexes formed direct the nucleophile to the allylic carbon atom which was previously substituted by the acetate leaving group. While we have no definitive explanantion for this, the work of Mealli and Musco and their co-workers may be significant.[122] They described the NMR spectral properties of $[(PPh_3)_2Pt(allyl)]X$ ($X = {}^-BF_4, {}^-OAc$) as being identical (at low temperature where static η^3-allyl complexes are present).

For the compounds $[(Cy_3P)_2Pt(allyl)]X$, ($X = {}^-BF_4, {}^-OAc$) they observed significantly different NMR spectra on changing between counter ions. This was proposed to be evidence that the acetate leaving group was still intimately involved with the allyl complex cation. It seems feasible that the reactions described here proceed through similar allyl complexes in which the acetate ion is not a simple "spectator" leaving group. It is difficult to explain the result obtained using *cis*-1,4-diacetoxy-2-butene, **(204)** as substrate, as a linear starting material was converted into a predominantly branched product providing tricyclohexylphosphine was used as the ligand. Although we have no evidence for this, one possible explanation is that acetate, **(204)** is not reactive under the reaction conditions, but undergoes equilibration *via* palladium catalysed rearrangement to a mixture of **(204),** and the branched regioisomer, $CH_2{=}CHCH(OAc)CH_2OAc$. This acetate could then undergo palladium catalysed allylic alkylation with some retention of regiochemistry.

Another possible explanation for the results we have obtained arises from observations made on the structure of $[(Cy_3P)_2Pt(C_3H_5)]PF_6$. NMR spectroscopic evidence suggested that each side of the allyl ligand is non-equivalent. This was proposed to be a result of the bulky PCy_3 ligands intermeshing in such a way that one ligand severely interacts with the allyl moiety, while the other does not.[142] If this were the case, the terminal allylic acetates would perhaps only bind with the least substituted end of the double bond cis to the "large" groups presented by one ligand.

If oxidative addition afforded an allyl complex that was attacked by the nucleophile more quickly than it could equilibrate, then a predominantly branched product may be expected from branched allylic acetates.

In summary, we attempted to develop a platinum catalysed double alkylation procedure, but discovered that the process was less straightforward, and less general, than we had envisaged. The effect of changing metal catalyst from palladium to platinum in the alkylation of four different unsymmetrical allylic acetates was also determined. The platinum catalysts generally show slightly improved selectivity towards products containing more electron poor double bonds than is observed with otherwise identical palladium catalysts. These studies led us to discover that a combination of tricyclohexylphosphine and $[(C_3H_5)MCl]_x$ (M = Pt, X = 4, M = Pd, X = 2) can give excellent regioselectivity in alkylations that proceed through unsymmetrical intermediates. Experiments that were designed to shed some light on the origin of this unusual effect have suggested that the reactions might proceed *via* $[(Cy_3P)_2Mallyl]^+ AcO^-$ complexes in which the acetate remains intimately involved with the allyl ligand. These catalysts could uncover further nuances in the mechanism of allylic alkylation, and allow synthetic chemists to retain the regiochemistry of an allylic acetate in the alkylation products.

Chapter 5

Experimental

Experimental

General.

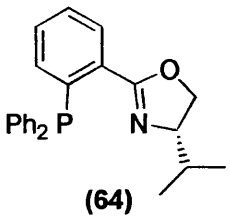
Commercially available reagents were used throughout without any purification. Unless stated all reactions were carried out under an atmosphere of nitrogen, while all work up and purification procedures were carried out in air. Solvents for reactions were of HPLC grade, whereas during work-up and purification, standard grade solvents were used. Where a solvent is described as dry, the standard grade solvent was distilled from an appropriate drying agent and stored under nitrogen over molecular sieves. Thin layer chromatography was carried out using aluminium backed plates coated with Merck Kieselgel 60 GF 254. Plates were visualised using U.V. light and / or permanganate dip. Flash chromatography was carried out using Merck Kieselgel 60H silica. Pressure was applied via hand bellows. Optical rotations were measured using an Optical activity AA10 automatic polarimeter, and are measured in 10^{-1} deg cm^2 g^{-1}. Infra red spectra were recorded as Nujol mulls on a Nicolet FTIR spectrometer with Phillips 7CM 3209 processor. Melting points were measured on a Gallenkamp single stage apparatus, and are uncorrected. Elemental analyses were conducted on a Carbo Erba Stametazione EA1506 analyser. ^{1}H, ^{13}C, ^{31}P and ^{195}Pt NMR spectra were recorded using a Jeol GX400 instrument. Crystal stuctures were obtained using a CAD 4 automatic 4 circle diffractometer. Metal complexes of (4*S*)-2-(2-Diphenylphosphinophenyl)-4-isopropyl-1,3-oxazoline are listed using the abbreviation, (*S*)-P^N.

The following compounds were purchased and used as received unless stated: (other routine chemicals not mentioned here were also purchased and used as received)

Potassium tetrachloroplatinate (II) (Aldrich), platinum (II) chloride (Aldrich), silver(I) tetrafluoroborate (Aldrich), tin(II) dichloride (Aldrich), silver(I) triflate (Aldrich), acetyl chloride (Aldrich), ethyl diazoacetate (Aldrich), hydrogen peroxide (35 % solution) (Merck), 1-octene (Aldrich), *N*-α-diphenylNitrone (Lancaster), styrene (Lancaster), *N*-benzylidenebenzylamine (Aldrich), methyl isocyanoacetate (Aldrich), benzaldehyde (Aldrich), di-isopropylethyl amine (Aldrich, distilled), triethylamine (Merck, distilled) acrylonitrile (Merck), 2-chloro-acrylonitrile (Aldrich), dicyclopentadiene (Aldrich)
methyl vinyl ketone (Aldrich), ethyl cyanoacetate (Aldrich), trifluoroacetyl chloride (Aldrich)
All of the phosphine ligands (Aldrich) except (S)-P^N
trifluoromethyl bromide (Aldrich), trimethylsilyltrifluoromethane (Lancaster), tetrabutyl ammonium bromide (Aldrich), (ethylene)-bis-triphenylphosphine-platinum(0) (Aldrich), dimethyl malonate (Aldrich), methyl dimethylmalonate (Aldrich), sodium (trimethoxy)-borohydride (Aldrich), *trans*-stilbene (Aldrich, benzylamine (Aldrich), phenol (recrystallised) (Aldrich), (R,R)-chiraphos (Aldrich), cyclohexen-2-ol (Aldrich), 2-chloroallyl acetate (Aldrich), cinnamyl acetate (Aldrich), 3-buten-2-ol (Aldrich), 1-hexen-3-ol (Aldrich), *trans*-2-hexenyl acetate (Lancaster), *cis*-1,4-diacetoxybut-2-ene (Aldrich), cyclohexenone (Aldrich), α-bromo-cinnamldehyde (Acros)

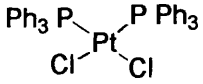
The following compounds were prepared by literature procedures.

(4*S*)-2-(2-Diphenylphosphinophenyl)-4-isopropyl-1,3-oxazoline [80].

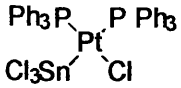


(64)

***cis*-Bis(triphenylphosphine) platinum(II) dichloride** [143]

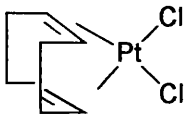


***cis*-Bis(triphenylphosphine)-trichlorostannyl-(chloro)-platinum (II)** [56]

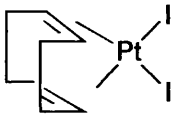


(69)

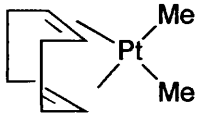
(1,5-Cyclo-octadiene)-dichloro-platinum (II) [57]



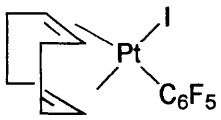
(1,5-Cyclo-octadiene)-diiodo-platinum (II) [57]



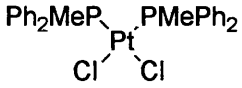
Dimethyl (1,5-cyclo-octadiene) platinum (II) [5]



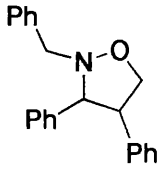
(1,5-Cyclo-octadiene)-iodo-(pentafluorophenyl)-platinum (II) [47]



***cis*-(Bis)-diphenylmethylphosphine-platinum (II) dichloride** [75]

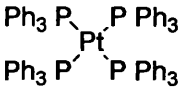


2-Benzyl-3-phenyl-4-phenylisooxazolidine [66]

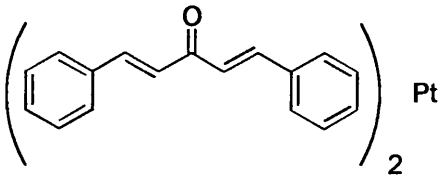


(29)

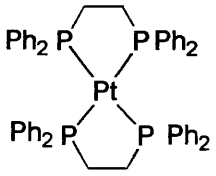
Tetrakis(triphenylphosphine)platinum (0) [144]



Bis-(dibenzylideneacetone)platinum(0) [104]



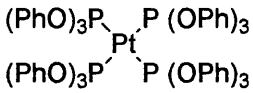
Bis-(bis-diphenylphosphinoethane)platinum (0) [145]



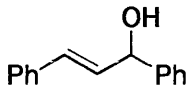
Tetrakis(chloro-allylplatinum)II [146]

$[(\eta^3\text{-}C_3H_5)PtCl]_4$

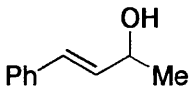
Tetrakis(triphenylphosphite)platinum(0) [144]



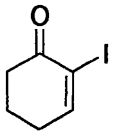
1,3-diphenylpropen-3-ol [115]



1-phenyl-3-methyl prop-2-en-3-ol [132]

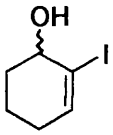


2-iodo-cyclohex-2-en-6-one [127]

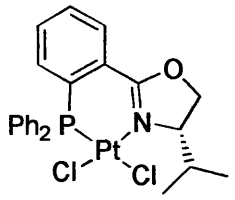


(181)

1-iodocyclohex-1-en-6-ol [127]



[(*S*)-P^N]$PtCl_2$, (66)

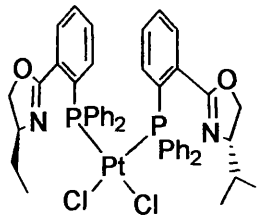


(66)

A 50 ml round bottom flask was charged with potassium tetrachloroplatinate (0.300 g, 0.723 mmol) and (4*S*)-2-(2-diphenylphosphinophenyl)-4-isopropyl-1,3-oxazoline (0.268 g, 0.716 mmol) and a magnetic stirring bead. The flask was then fitted with a reflux condensor equipped with a rubber septum and flushed with nitrogen. Dry acetonitrile (15ml) was then added using a syringe, and the suspension was heated under reflux for six hours, by which time the potassium tetrachloroplatinate had disappeared. The reaction was then left to stir overnight. At the end of this period the solvent was reduced to 1 ml *in vacuo* and ether added to yield a pale yellow, air stable precipitate containing two compounds, **(66)** and **(67)**. ^{31}P NMR (161.7 MHz; $CDCl_3$) δ**(67)**: 5.8, $^1J_{P\text{-}Pt}$ =3410 Hz; **(66):** 0.51, $^1J_{P\text{-}Pt}$=3722 Hz; ^{195}Pt NMR (161. 7 MHz, $CDCl_3$) δ **(67):** -4200, br t, $^1J_{Pt\text{-}P}$ =3410-3425 Hz; **(66):** -3550, br, dm, $^1J_{Pt\text{-}P}$=3660- 3700Hz. These two compounds are separated from each other by flash chromatography using 99%DCM / 1%MeOH as eluent (R_f **(66)**~ 0.35; R_f **(67)** ~ 0.05). The desired product is that which comes off the column first. (Yield: 0.371 g, 0.58 mmol, 81 %). Recrystallisation from chloroform/toluene gives yellow prisms suitable for X- ray diffraction. (Found: C, 44.7; H, 3.69; N, 2.13. $C_{24}H_{24}Cl_2NOPPt$ requires: C, 45.05; H, 3.75; N, 2.19). M.p > 250 °C. $[\alpha]_D^{20}$ = +183.8 (c = 1.9, $CHCl_3$); υ_{max}/cm^{-1} 1622,1103, 954, 929, 752. ^{31}P NMR (161. 7 MHz, $CDCl_3$) δ 0.51 ($^1J_{P\text{-}Pt}$=3722 Hz);

^{195}Pt NMR (161.7 MHz; $CDCl_3$)δ: -3550 (br, dm, $^1J_{Pt-P}$ ≅3660 Hz); ^{1}H NMR (400 MHz; $CDCl_3$)δ: 0.13 (3H, d, ^3J = 7.0 Hz, C**H**$_3$), 0.83 (3H, d, ^3J= 7.0 Hz, C**H**$_3$), 2.72-2.78, (1H, m, C**H**$(CH_3)_2$), 4.46-4.51 (2H, m, C**H**$_2$O), 5.78 (1H, m, C**H**N), 7.00 (1H, dd, J=10.1,7.9, ArH), 7.38-7.71 (12H, m, ArH), 8.12 (1H, m, ArH).

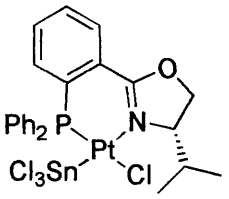
[(*S*)-P^N]$_2$PtCl$_2$, (67)



(67)

A solution of **[(*S*)-P^N]PtCl$_2$** in $CDCl_3$ (0.040 g, 0.063 mmol in 0.6 ml $CDCl_3$) was added to vial containing (4*S*)-2-(2-diphenylphosphinophenyl)-4-isopropyl-1,3-oxazoline (0.023g, 0.063 mmol). The vial was shaken until a solution was obtained, which was added to an NMR tube for NMR analysis. Evaporation of solvent gives a yellow powder which is brighter in colour than the starting material. (Yield: 0. 62g, 0.063 mmol, 100%). ^{31} P NMR (161.7 MHz; $CDCl_3$) δ: 5.8, $^1J_{P-Pt}$ =3410 Hz; ^{195}Pt NMR (161. 7 MHz, $CDCl_3$) δ: -4200, br t, $^1J_{Pt-P}$ =3410-3425 Hz; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.01 (3H, d, ^3J = 6.7 Hz, C**H**$_3$), 0.76 (3H, d, ^3J= 6.7 Hz, C**H**$_3$), 1.80, (1H, m, C**H**$(CH_3)_2$), 4.37 (1H, dd, app., ^3J = 10.0, 3.5 Hz, CH**H**O), 4.59 (1H, m, C**H**HO), 5.50 (1H, t, app., ^3J = 9.7 Hz C**H**N), 6.7- 8.1 (14H, m, ArH).

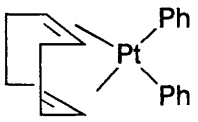
[(*S*)-P^N]Pt($SnCl_3$)Cl, (68)



(68)

A solution of vacuum dried tin dichloride (0.040 g, 0.21 mmol) in dry acetone (4 ml) was added *via* syringe to a stirred solution of [(*S*)-P^N]$PtCl_2$, (0.134 g, 0.21 mmol) in dry DCM (5 ml). This was then stirred overnight. The resultant orange precipitate was then filtered off, dissolved in DCM, filtered and dried *in vacuo* to give the desired product. Yield: 0.162g, 0.196 mmol, 94 %. (Found: C, 34.90; H, 3.16; N, 1.62; $C_{24}H_{24}Cl_4NOPPtSn$ requires: C, 34.75; H, 2.90; N, 1.69). υ_{max}/cm^{-1} : 1630, 1251. ^{31}P NMR (161.7 MHz; $CDCl_3$) δ: 4.27 ($^1J_{P\text{-}Pt}$=3541 Hz, $^2J_{P\text{-}Sn}$=156 Hz). ^1H NMR (400 MHz; $CDCl_3$) δ: -0.05 (3H, d, ^3J = 7 Hz, C**H**$_3$), 0.70 (3H, d, ^3J=7 Hz, C**H**$_3$), 2.25 (1H, m, C**H**$(CH_3)_2$), 4.45 (2H, m, C**H**$_2$O), 5.50 (1H, m, C**H**N), 6.85 (1H, dd, ^3J=11.9, 7.63 Hz, Ar**H**), 7.28-7.7 (12H, m, Ar**H**), 8.12 (1H, dd, ^3J=7.5, 3.8 Hz).

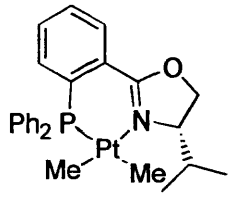
Diphenyl (1,5-cyclo-octadiene) platinum (II), (73)



This was prepared by a slight modification to the literature procedure.[57a] Phenylmagnesium bromide, (2.8 ml of a 3M solution in toluene, 7 mmol) was transferred *via* a syringe into a suspension of cyclo-octadiene-diiodo-platinum (II), (0.98 g, 1.76 mmol) in dry toluene, (17 ml). The bright yellow suspension went

brown instantly. This mixture was stirred at room temperature for 30 minutes, then neutralised with 0.6 g of ammonium chloride in 10 ml of ice cold water. The organic layer was separated, with the aqueous layer being extracted a further two times with toluene. Organic extracts were combined, dried with sodium sulphate, and decolourised with charcoal. Solvent was then removed *in vacuo*. The white precipitate was purified by flash chromatography on silica (pre-treated with triethylamine) using 20% ether/ 80% petrol ether (40 / 60) as eluent (R_f **(73)** ~ 0.5; R_f (impurity)~ 0.2) . Yield: 0.683 g, 1.49 mmol, 85 %. (Found: C, 51.8; H, 4.97; $C_{20}H_{18}Pt$ requires: C, 52.5; H, 4.81)

[(*S*)-P^N] $PtMe_2$, (74)

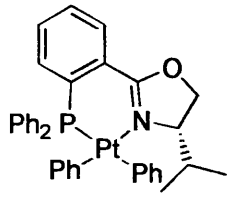


(74)

A solution of ligand **(64)** (196 mg, 0.584 mmol) in dry toluene (6 ml) was slowly added over six hours to a stirred solution of dimethyl (1,5-cyclooctadiene) platinum (II) (218 mg, 0.584 mmol) in dry toluene (6 ml) at 50 °C. The reaction was stirred at 50 °C for a further 10 hours after addition was complete. The reaction was then cooled to room temperature. The solvent, and most of the 1,5-cyclooctadiene was removed *in vacuo* at 40 °C. The yellow crystals that formed were washed with cold absolute EtOH, (2 x 4 ml) using a syringe. The washed crystals were dissolved in DCM, filtered, and dried *in vacuo*. Yield: 0.346 g, 0.578 mmol, 98 %.

(Found: C, 52.19; H, 5.03; N, 2.16. $C_{26}H_{30}NOPPt$ requires: C, 52.17; H, 5.05; N, 2.34). $[\alpha]_D^{20} = +143.1$ (c = 1.16, $CHCl_3$) υ_{max}/cm^{-1} 1622, 1435, 1366, 1237, 1105, 1098, 1055, 747, 695. ^{31}P NMR (161.7MHz; $CDCl_3$) δ: 21.29, $^1J_{P\text{-}Pt}$=1972 Hz; ^1H NMR (400 MHz; $CDCl_3$) δ: 0.04 (3H, d, ^3J=7.0 Hz, $CH(CH_3)_2$), 0.51 (3H, d, $^3J_{H\text{-}P}$=7.6 Hz, $^2J_{H\text{-}Pt}$=87.14 Hz, CH_3-Pt-N), 0.61 (3H, d, $^3J_{H\text{-}P}$=7.6 Hz, $^2J_{H\text{-}Pt}$=68.1 Hz, CH_3-Pt-P), 0.82, (3H, d, ^3J=7.3 Hz, $CH(CH_3)_2$), 2.5 (1H, m, $CH(CH_3)_2$), 4.24 (2H, m, CH_2O), 4.88 (1H, m, CHN), 6.9-8.0, (14 H, m, ArH).

[(*S*)-P^N] $PtPh_2$, (75)

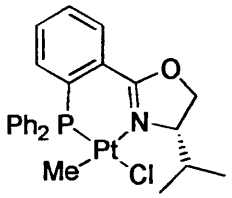


(75)

To a stirred solution of diphenyl (1,5-cyclo-octadiene) platinum (II), (0.609 g, 1.33 mmol) in dry toluene (40 ml) was added a toluene solution of (4S)-2-(2-diphenylphosphinophenyl)-4-isopropyl-1,3-oxazoline, (0.493 g, 1.32 mmol in 9.2 ml solvent) over a period of twelve hours (*via* a syringe pump). This was left stirring overnight to yield a clear yellow solution. Solvent was removed *in vacuo* to give a yellow slurry. This was then dissolved in the minimum amount of DCM. Petroleum ether (60/80) was added until the solution started to go cloudy. This was left to crystallise into yellow prisms suitable for a crystal structure determination. Yield: 617 mg, 0.854 mmol, 65%. (Found: C, 59.6; H, 4.76; N, 1.92; $C_{36}H_{34}NOPPt$ requires: C, 59.8; H, 4.74; N, 1.94). $[\alpha]_D^{20} = +22.6$ (c = 2.35, $CHCl_3$);

m.p. = 215 °C (decomp.); υ_{max}/cm^{-1} 3046, 1634, 1570, 1248, 1097, 1055, 1024, 955, 739, 694. ^{31}P NMR (161.7 MHz; $CDCl_3$) δ: 18.23 $^1J_{P\text{-}Pt}$= 1849 Hz; ^1H NMR (400 MHz; $CDCl_3$) δ: 0.27 (3H, d, ^3J= 7.0 Hz, CH_3), 0.71 (3H, d, ^3J= 7.0 Hz, CH_3), 2.65 (1H, m, $CH(CH_3)_2$), 4.20 (1H, m, CHN), 4.40 (2H, m, CH_2O), 6.75 (3H, m, ArH), 7.10 (1H, m, ArH), 7.2-7.9 (17H, m, ArH), 8.05 (2H, m, ArH), 8.35 (1H, m, ArH).

[(*S*)-P^N] Pt(Me)Cl, (76)

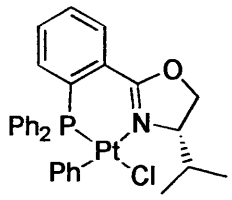


(76)

To a stirred solution of **[(*S*)-P^N] $PtMe_2$, (74)**, (0.320 g, 0.535 mmol) in dry methanol (2.3 ml) and dry DCM (3.5 ml) was added acetyl chloride (0.040 ml, 0.044 g, 0.562 mmol). This was stirred for two hours. The volume of solvent was then reduced to c. 0.3 ml *in vacuo*. The yellow precipitate was washed with hexane (2 x 1 ml) and collected using a Buchner funnel. This powder was then dissolved in DCM and filtered. Solvent was then removed from the filtrate, and the yellow powder dried *in vacuo* to give the desired product. (Yield: 0.268 g, 0.433 mmol, 81 %). Recrystallisation from DCM/ petroleum ether gave crystals suitable for X-ray diffraction. These single crystals contained some residual petroleum, as revealed by analysis and the X-ray study. (Found: C, 45.7; H, 4.21; N, 2.14. $C_{25}H_{27}ClNOPPt$ requires: C, 48.51; H, 4.40; N, 2.26). A week later these crystals collapsed to a yellow powder, which was almost analytically pure. (Found: C, 47.9;

H, 4.35; N, 2.24); $[\alpha]_D^{20} = +123$; υ_{max}/cm^{-1}: 1733, 1628, 1242, 1100, 953, 730, 696. ^{31}P NMR (161.7 MHz; $CDCl_3$) δ: 12.71, $^1J_{P\text{-}Pt}$= 4703 Hz. ^1H NMR (400 MHz; $CDCl_3$) δ: 0.07 (3H, d, ^3J= 6.7 Hz, $CH(CH_3)_2$), 0.52 (3H, d, $^3J_{H\text{-}P}$=3.4 Hz, $^2J_{H\text{-}Pt}$=72.6 Hz, CH_3-Pt-N), 0.83 (3H, d, ^3J= 7.3 Hz, $CH(CH_3)_2$), 2.74 (1H, m, $CH(CH_3)_2$), 4.45 (2H, m, CH_2O), 5.50 (1H, m, CHN), 7.0-8.3 (14H, m, ArH).

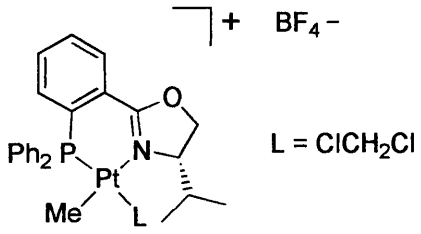
[(*S*)-P^N] Pt(Ph)Cl, (77)



(77)

To a stirred solution of**[(*S*)-P^N] $PtPh_2$, (75)**, (0.178 g, 0.246 mmol) in dry methanol (1.3 ml) and dry DCM (2.5 ml) was added acetyl chloride (0.019 ml, 0.266 mmol). This was stirred for 30 minutes. The resultant pale yellow solution was filtered. Solvent was then removed from the filtate, and the pale yellow powder was dried under high vacuum. Yield: 150 mg, 0.202 mmol, 89 %. (Found: C, 53.1; H, 4.65; N, 1.83; $C_{30}ClH_{29}NOPPt$ requires: C, 52.9; H, 4.29; N, 2.06) $[\alpha]_D^{20}$= +51.4 (c = 1.4, $CHCl_3$); m.p. = 177 °C; υ_{max}/cm^{-1} 1734, 1625, 1570, 1243, 1099, 730, 694; ^{31}P NMR (161.7 MHz; $CDCl_3$) δ 8.1, $^1J_{P\text{-}Pt}$ = 4637 Hz. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.11 (3H, d, ^3J= 6.7 Hz, $CH(CH_3)_2$), 0.70 (3H, d, ^3J= 6.7 Hz, $CH(CH_3)_2$), 2.5 (1H, m, $CH(CH_3)_2$), 4.22 (2H, m, CH_2O), 5.55 (1H, m, CHN), 6.35 (3H, m, ArH), 6.73 (2H, m, ArH), 6.80- 7.5 (11H, m, ArH), 7.70 (2H, m, ArH), 7.95 (1H, m, ArH).

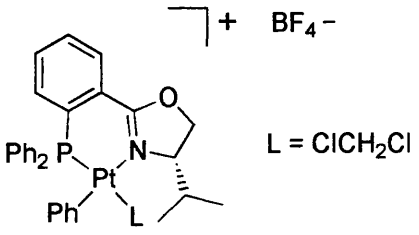
[(*S*)-P^N) Pt(Me)CH_2Cl_2] BF_4, (78)



(78)

To a stirred solution of **[(*S*)-P^N] Pt(Me)Cl, (76),** (0.176 g, 0.285 mmol) in dry DCM was added silver tetrafluoroborate, (0.056 g, 0.287 mmol) in one portion. The flask was then flushed with nitrogen, and stirred in the dark for an hour. The resulting suspension was then filtered under nitrogen using a filter cannula. The solution obtained had its solvent removed and was dried under high vacuum. Yield: 0.167 g, 0.221 mmol, 78 %. (Found: C, 41.9; H, 4.20; N, 1.87. $C_{26}H_{29}BCl_2F_4NOPPt$ requires: C, 41.37; H, 3.88; N, 1.86). $[\alpha]_D^{20}$ 80.0 (c = 1.56, $CHCl_3$); m.p. = 214 °C (decomp.); υ_{max} /cm^{-1}: 3363, 2287, 1631, 1584, 1567, 1258, 1101, 1063, 998, 955, 732, 693; ^{31}P NMR (161.7 MHz; $CDCl_3$) δ: 8.46, $^1J_{P\text{-}Pt}$=5263 Hz. ^1H NMR (400 MHz; $CDCl_3$) δ: 0.20 (3H, d, ^3J=6.7 Hz, CH**Me**$_2$), 0.34 (3H, s, ^2J = 63.2 Hz, C**H**$_3$-Pt-P), 0.80 (3H, d, ^3J = 7.0 Hz, CH**Me**$_2$), 2.32 (1H, m, C**H**Me$_2$), 4.34 (1H, dd, ^3J = 8.9 Hz, ^3J = 4.3Hz, C**H**O), 4.60 (1H, t-app., ^3J = 9.2 Hz, C**H**O) 4.80, 1H, m, C**H**N), 5.61 (2H, s, br, [co-ord. DCM]), 7.0-8.2 (14H, m, Ar**H**).

[(*S*)-P^N) Pt(Ph)CH_2Cl_2] BF_4, (79)



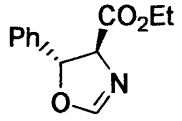
(79)

To a stirred solution of [(*S*)-P^N] Pt(Ph)Cl, (77), (0.119 g, 0.175 mmol) in dry DCM (6 ml) was added silver tetrafluoroborate, (0.034 g, 0.175 mmol) in one portion. The flask was then flushed with nitrogen, and stirred in the dark for an hour. The resulting suspension was filtered through a pad of Celite. Solvent was removed from the filtrate, and the pale powder obtained was dried under high vacuum. Yield: 0.113g, 0.138 mmol, 79%. ^{31}P NMR (161.7MHz; $CDCl_3$) δ: 3.89 (^1J = 5198 Hz) ^1H NMR (400 MHz; $CDCl_3$) δ: 0.34 (3H, d, ^3J = 6.7 Hz, CH**Me**$_2$), 0.85 (3H, d, ^3J = 6.9 Hz, CH**Me**$_2$), 2.33 (1H, m, C**H**Me$_2$) 4.40 (1H, m, C**H**O), 4.78, 2H, m, C**H**O & C**H**N), 5.8 (1H, br, s, co-ord. DCM?) 6.6-8.4, (ArH). Impurities: (c. 30% w.r.t. major prod.) ^{31}P NMR (161.7MHz; $CDCl_3$) δ: 5.14 (^1J = 5075 Hz) ^1H NMR (400 MHz; $CDCl_3$) δ: 0.10, d, 6.67 Hz; 0.74, d, 6.67Hz; 1.70, s, br; 2.46, m; 4.03, m; 4.35, m; 6.4-8.2, m, ArH. MS. (m/z) (F.A.B.) 645.1647 (M-BF_4.CH_2Cl_2)+ req.s 645.1634);

General procedure for compounds 92 a-e.

To a flask containing compound **(78)**, (10 mg, 0.013 mmol) was added a solution of organic ligands **a-e**, (0.016 mmol, 1.2 eq. in 0.5 ml $CDCl_3$). The resulting solution was then added *via* a syringe to an NMR tube and the NMR spectrum measured. Selected resonances are noted in Table 3.

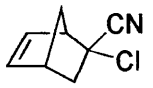
4-(Methoxycarbonyl)-5-phenyl-2-oxazoline, (96) from aldol reaction of methyl isocyanoacetate and benzaldehyde.[147]



(96)

To an evacuated round-bottomed flask containing the platinum catalyst, **(78)** (14.6 mg, 0.02 mmol, 2 mol%) and a stirring bead was added HPLC DCM (7 ml), nitrogen, methyl isocyanoacetate (0.092 ml, 99 mg, 1 mmol), benzaldehyde (0.102 ml, 0.106 g, 1mmol) and Hünigs base (0.022 ml, 0.13 mmol, 13 mol%) in that order. The flask was stirred at 20 °C until T. L. C revealed complete conversion, as monitored by disappearance of methyl isocyanoacetate (R_f ~ 0.7, 50 % EtOAc/ petroleum ether, MnO_4- or PMA dip). The *cis* and *trans* products were obtained as a mixture after column chromatography on silica using 50% EtOAc / Petroleum ether as eluent (R_f (*cis*) ~ 0.5, R_f (*trans*) ~ 0.45). Combined yield of both isomers: 0.191 g, 0.94 mmol, 94 %). ^{1}H NMR revealed the compound isolated to be a mixture of *cis* and *trans*- 4-(methoxycarbonyl)-5-phenyl-2-oxazoline by comparison with literature NMR data.[147] *cis / trans* = 70:30. For some reason, I could not isolate the *trans* isomer in pure form (it was always contaminated with the cis product). ^{1}H NMR (400 MHz; $CDCl_3$) δ: (*trans*-**(96)**) 3.76 (3H, s, CO_2**Me**) 4.55 (1H, dd, ^{3}J = 7.8, 2.2 Hz, CHC**H**O), 5.62 (1H, d, ^{3}J = 7.7 Hz, PhC**H**CH), 7.05 (1H, d, ^{3}J = 2.2 Hz, **H**C=N) 7.2-7.4, (5H,m, Ar**H**). δ: (*cis*, **(97)**) 3.1, (3H,s, CO_2**Me**), 4.95 (1H, dd, ^{3}J = 11.0, 2.2 Hz, CHC**H**O), 5.62 (1H, d, ^{3}J = N / D, PhC**H**CH), 7.0-7.4 (6H, m, **H**C=N & Ar**H**).

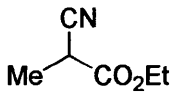
***endo*-2-Chlorobicyclo[2.2.1]hept-5-ene-2-(*exo*)-carbonitrile, (100)** [72]



(100)

To an evacuated round bottomed flask containing, catalyst **(78)** (25 mg, 0.0331 mmol), and a stirring bead was added DCM (2.5 ml) and 2-chloro-acrylonitrile (58 mg, 0.662 mmol). This flask was then flushed with nitrogen. Cyclopentadiene (0.220 g, 3.31 mmol) was then added, and the reaction vessel was stirred at a given temperature (25 °C, 0 °C, or -15 °C) until the reaction had gone to completion. The progress of the reaction was followed by G.C. The ENDO/EXO ratio and the enantioselectivity were also determined by G.C.[73] When the reaction was complete, DCM (4 ml) was added, and the reaction mixture was filtered through a pad of silica. The resultant solution had its solvent removed to give a colourless oil which solidified on standing. The major isomer was identified as *endo*-2-chlorobicyclo[2.2.1]hept-5-ene-2-(*exo*)-carbonitrile by comparison of its NMR spectra with the literature.[72] ^{1}H NMR (400 MHz, $CDCl_3$) (major *endo*-2-chloro isomer) δ: 1.70 (1H, dd, ^{3}J = 13.1, 3.1 Hz, HC**H**CCN) 1.71 (2H, brs, C**H**$_2$), 2.70 (1H, dd, ^{3}J = 13.1, 3.7 Hz, **H**CHCCN), 3.09 (1H, br, s, C**H**CH$_2$ (bridgehead)) 3.49 (1H, brs, C**H**CH$_2$ [bridgehead]), 6.11 (1H, dd, ^{3}J = 5.7, 3.1 Hz, =C**H**), 6.41 (1H, dd, ^{3}J = 5.7, 3.1 Hz, =C**H**); ^{13}C NMR (67.80 MHz) δ: 42.86, [-**C**H-(bridgehead)]; 45.67, [-**C**H$_2$-]; 48.51, [-**C**H$_2$-]; 55.35, [-**C**H- (bridgehead)]; 56.1, [**C**(Cl)CN]; 121.4, [-**C**N]; 131.97, [=**C**H]; 139.38, [=**C**H]. (MS, CI+) m/z: MH+: 154.0)

Ethyl-2- cyano-propionate, (103) [148]



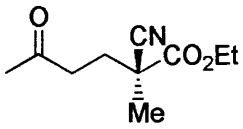
(103)

A more efficient synthesis of compounds of this type has been published, [148] but we happened to have the reagents for the following synthesis in store.

The reaction was only run once, and hence the yield is not optimised. A solution of sodium ethoxide (9.024 g, 0.133 mol) in ethanol, (60 ml) was added dropwise, *via* an addition funnel, to a stirring solution of ethyl cyanoacetate (15 g, 14.11 ml, 0.133 mol) in ethanol (60 ml). Once addition is complete, the reaction was cooled to 0 °C. Methyl iodide (19.63 g, 8.611 ml, 0.138 mol) is carefully added via syringe, and the reaction stirred for two hours.. Solvent was removed from the reaction flask, and the residue was extracted with ether (100 ml) and washed with water (2 x 100 ml). The organic extracts were dried ($MgSO_4$), and filtered. The solvent was removed from the filtrate to yield the crude product, which was purified by column chromatography using 30% ether/petrol as eluent [R_f **(103)** ~ 0.3; R_f (S. M.) ~ 0.15; R_f (impurity) ~ 0.4]. This column was carried out using only a portion of the crude product. The average yield from the column was 37 %.

υ_{max} /cm^{-1}: 3475, 2988, 2949, 2912, 2253, 1747, 1458, 1383, 1369, 1300, 1270, 1200, 1110, 1034, 862; ^{1}H NMR (270 MHz) δ: 1.33 (3H, t, ^3J = 7.1 Hz, CH_2CH_3), 1.60 (3H, d, ^3J = 7.3 Hz, $CHCH_3$), 3.57 (1H, q, ^3J = 7.3 Hz, $CHCH_3$) 4.27, 2H, q, ^3J = 7.1 Hz, CH_2CH_3). ^{13}C NMR (67.80 MHz) δ: 166.44, [-CO_2-]; 117.29, [-CN]; 62.73, [CH_2CH_3] ; 31.412, [$CHCH_3$]; 13.816, [CH_2CH_3]. (MS, CI+): MH+: 128.0;

5-(Carboethoxy)-5-cyano-hexan-2-one, (104).[74]



(104)

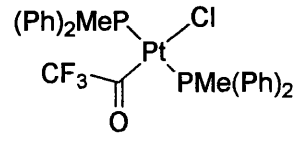
To an evacuated one-necked round bottomed flask containing catalyst **(78)** (7.6 mg, 0.01 mmol) and a stirring bead was added a solution of ethyl cyanopropionate (0.127 g, 1 mmol) in dry solvent (4 ml). This flask was then flushed with nitrogen. Hünigs base (0.017 ml, 13 mg, 0.1 mmol) and methyl vinyl ketone (0.125 ml, 0.105 g, 1.5 mmol) were then syringed into the flask. (on some occasions methyl vinyl ketone was added as a solution in 3 ml solvent using a syringe pump at its slowest setting) The reaction was then stirred at room temp. Reaction progress was assessed by T.L.C. (The product has an R_F of 0.15 in 35% ether / petrol; $KMnO_4$ dip). When the reaction was complete, solvent (and excess methyl vinyl ketone) was removed *in vacuo,* and the pure product, **(104)** obtained after column chromatography using 30 % ether / petrol as eluent (yields are given in the table). The compound was identified by comparison of its NMR data with literature values.[74]

^{1}H NMR (400 MHz) δ: 1.34 (3H, t, ^3J = 7.1 Hz, $CH_2C\mathbf{H_3}$), 1.61 (3H, s, NC-C-$C\mathbf{H_3}$), 2.0-2.3 (2H, m, CH_2-$C\mathbf{H_2}$-C-), 2.19 (3H, s, $C\mathbf{H_3}$-CO), 2.5-2.8 (2H, m, C(O)-$C\mathbf{H_2}$-) 4.27 (2H, q, ^3J = 7.1 Hz, $C\mathbf{H_2}CH_3$). ^{13}C NMR (67.8 MHz) δ: 13.90, 23.43, 29.90, 31.46, 39.12, 43.02, 62.87, 119.46, 168.79. 205.74; (MS, CI+): MH+ 198.1.

General procedure for catalytic epoxidation testing

0.1 mmol of catalysts **(78), (79), (66)** with 0.1 mmol $SnCl_2$ and **(66)** with 0.1 mmol $AgBF_4$ were placed in separate flasks. A stirring bead was placed in each flask which were then stoppered, evacuated, flushed with nitrogen, and placed in a water bath at 18 °C. Degassed HPLC grade DCM, (5 ml), and 1-octene, (0.7 ml, 4.4 mmol), were then added and the reaction mixtures were stirred in the water bath. A fifth reaction flask containing only DCM, octene, and H_2O_2 was also set up as a control. 35 % hydrogen peroxide solution (0.8 ml, 5 mmol) was then added via syringe. After 4, 24, and 72 hours, 0.1 ml of the reaction mixture were removed from each flask, dissolved in 1 ml of DCM, and filtered through a short plug of silica and analysed by gas chromatography. Another solution of 99 % octene and 1 % epoxide was also worked up in this way to confirm that the analytical method could detect down to 1 % conversion.

***trans*-Bis-(diphenylmethylphosphine)-chloro-(trifluoroacetyl) platinum (II), (109)** [75]

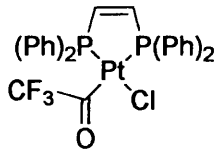


(109)

Trans-bis (diphenylmethylphosphine) chloro (trifluoroacetyl) platinum (II) was prepared by the method first described by Bennett et.al.[75] Its preparation is given here as the original paper does not contain a detailed experimental section.

A solution of diphenylmethylphosphine, (1.55 ml, 1.83 mmol) in 95% ethanol, (15 ml) was syringed into a schlenk tube containing a suspension of *cis*-diphenylmethylphosphine-platinum (II) dichloride, (2.28 g, 3.42 mmol) in 45 ml of ethanol. This was stirred for 10 minutes, after which a solution of potassium hydroxide, (0.46 g, 8.13 mmol) in 80/20 ethanol/water was added. This mixture was then stirred at 60 °C under an atmosphere of nitrogen (no condensor is required). After four hours, the resultant yellow solid was filtered off under nitrogen, washed with water and ethanol and then transferred to a schlenk tube containing a magnetic stirring bead where it was dried *in vacuo*. HPLC grade hexane, (55 ml) was then added *via* syringe, before the tube was evacuated and flushed several times with nitrogen. Trifluoroacetyl chloride gas was then bubbled into the suspension until the yellow colour had gone (about 2 minutes). The gas was added via standard, dry, tubing and a syringe which was submerged into the suspension. Any excess gas above the suspension was allowed to travel *via* a cannula to a flask of propan-2-ol. Excess gas from here diffused through another cannula to a flask of methanol, which was itself open to diffuse into a flask of sodium hydroxide. This is probably a bit over the top, but is does ensure that all traces of this highly toxic gas are removed. The reaction mixture was left to stir for an hour, while the system was flushed with nitrogen. The white precipitate was filtered off, in air, and washed with a small amount of hexane and ethanol. (Yield: 1.26 g, 1.74 mmol, 51 %) Its identity is confirmed by comparison of NMR data with literature values.

Vinyldiphenylphosphine-chloro-(trifluoroacetyl) platinum (II), (110)



(110)

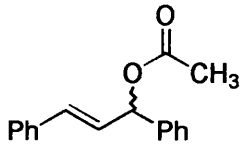
A solution of vinyldiphenylphosphine, (0.067 g, 0.19 mmol) in dry toluene, (3 ml) was slowly added to a boiling, stirred suspension of *trans*-bis (diphenylmethylphosphine)-chloro-(trifluoroacetyl)platinum (II), (0.138 g, 0.19 mmol) in 8 ml of toluene. This was heated under reflux for four hours. After cooling, solvent was reduced to 1 ml under vacuum and diethyl ether added. The resulting white precipitate was then filtered off and dried *in vacuo*. ^{31}P NMR indicated this to be a very impure sample. The correct product was obtained by flash chromatography using 32% ethyl acetate/petrol as eluent (R_f **(110)** ~ 0.45). (Yield: 0.67 g, 0.093 mmol, 47%) υ_{max}/cm^{-1} : 1749, 1662, 1240, 1101, 873; ^{31}P NMR (400 MHz; $CDCl_3$) 48.5 ($^1J_{P\text{-}Pt}$=1752 Hz, $^2J_{H\text{-}P}$+ $^4J_{H\text{-}P}$=9.9, +$^2J_{P\text{-}P}$=5.9), 40.37 ($^1J_{P\text{-}Pt}$= 3979 Hz, $^2J_{P\text{-}P}$= 5.9 Hz); ^1H NMR (400 MHz; $CDCl_3$) 1.2 (2H, t, ^3J =7.2Hz, **H**C=C**H**), 7.0-7.8, 20 H, m, ArH.

General procedure for the preparation of allylic acetates.

The allylic acetates used throughout chapters three and four were either purchased or prepared from the corresponding alcohols by the following general procedure. The majority of them are very well known compounds and were characterised by comparison of T.L.C and NMR data with authentic samples / literature values. They were further characterised by reacting as expected in palladium catalysed allylic alkylation reactions. ^1H NMR is given here for reference purposes.

A 50 ml, one-necked round bottomed flask was charged with a stirring bead, catalyst, and the allylic alcohol (5.4 mmol,1 equiv.). It was then stoppered and flushed with nitrogen. HPLC grade DCM was then added *via* a syringe (10 ml), and the reaction vessel was cooled to 0 °C. A few crystals of 4-dimethylamino-pyridine were then added. The flask was restoppered prior to the addition of triethylamine *via* syringe (0.75 ml, 55g, 5.4 mmol, 1 equiv.). An excess of acetic anhydride was then added, also *via* syringe (1.02 ml, 1.10 g, 10.8 mmol, 2 equiv.). The reaction vessel was stirred at room temperature until T. L. C. analysis showed complete consumption of the starting alcohol. This is typically about four hours. The reactions were then diluted with DCM and washed with water. The aqueous layer was washed with more DCM, and the organic extracts were combined and washed with water and then brine. After drying ($MgSO_4$) and evaporation of solvent, the acetate can be obtained pure enough for our purposes by drying under high vacuum. [Column chromatography of some allylic acetates results in decomposition].

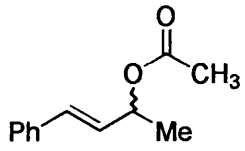
(*E*)-1,3-Diphenyl-prop-2-enyl acetate, (112)



(112)

R_f ~ 0.6 (30 % Et_2O / petroleum ether) ^1H NMR (400 MHz; $CDCl_3$, 20°C): δ: 2.08 (3H, s, CO_2**Me**); 6.30-6.5 (2H, m, 2 x C**H**), 6.66 (1H, d, ^3J = 15.6 Hz, C**H**); 7.2-7.4 (10H, m, Ar**H**).

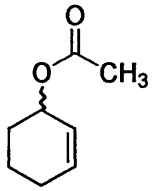
(E)-3-Acetoxy-1-phenyl-1-butene, (194)



(194)

R_f ~ 0.6 (30 % Et_2O / petroleum ether) ^1H NMR (400 MHz; $CDCl_3$, 20 °C) δ: 1.35 (3H, d, ^3J = 6.0 Hz, CHC**H**$_3$) 1.97 (3H, s, CO_2C**H**$_3$), 5.45 (1H, qn, ^3J = 6.0 Hz, C**H**CH$_3$), 6.00, (1H, dd, ^3J = 6.0, 16.0 Hz, =C**H**CH), 6.50, (1H, d, ^3J = 16.0 Hz, **H**C=CH), 7.0-7.5 (5H, m, Ar**H**).

2-cyclohexen-1-ylacetate, (159)

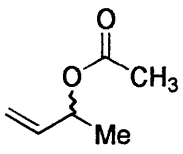


(159)

This reaction was carried out at 35 °C for 5 hours.

R_f ~ 0.8 (30 % Et_2O / petroleum ether) ^1H NMR (400 MHz; $CDCl_3$, 20°C) δ: 1.60-2.07 (6H, s, 3 x C**H**$_2$), 2.05 (3H, s, CO_2C**H**$_3$), 5.26 (1H, m, C**H**OAc), 5.70 (1H, m, **H**C=CH), 5.95 (1H, m, HC=C**H**).

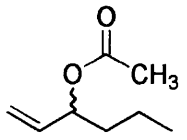
But-2-enyl acetate, (125)



(125)

R_f ~ 0.8 (30 % Et_2O / petroleum ether) ^1H NMR (400 MHz; $CDCl_3$, 20°C) δ: 1.25 (3H, d, ^3J = 6.6 Hz, C**H**$_3$CH), 2.20 (3H, s, CO_2**Me**), 5.07 (1H, dt, ^3J = 10.5, 1.4 Hz, HC=C**H**H), 5.28 (1H, m, HC=CH**H**), 5.78 (1H, ddd, ^3J = 5.9, 10.5, 17.4 Hz, C**H**=CHH).

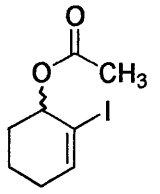
1-Hexen-3-yl acetate, (197)



(197)

R_f ~ 0.9 (30 % Et_2O / petroleum ether) ^1H NMR (400 MHz; $CDCl_3$, 20 °C) δ: 0.84, (3H, t, ^3J = 7.3 Hz, C**H**$_3$CH$_2$), 1.26 (2H, m, CH$_3$C**H**$_2$), 2.0 (3H, s, CO_2**Me**), 5.14 (3H, m, C**H**OAc, & CH=C**H**$_2$), 5.70 (1H, hept.-app., ^3J = 6.4, 10.6, 17.4 Hz, C**H**=CH$_2$).

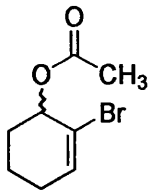
1-Iodo-cyclohex-2-enyl acetate, (182)



(182)

R_f ~ 0.7 (20 % Et_2O / petroleum ether) ^1H NMR (400 MHz; $CDCl_3$, 20 °C) δ: 1.65-2.20 (6H, m, 3 x C**H**$_2$); 2.11 (3H, s, CO_2**Me**), 5.38 (1H, t, ^3J = 4.6 Hz, C**H**OAc), 6.63 (1H, t, ^3J = 4.4 Hz, C**H**Cl).

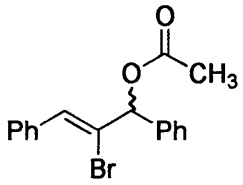
1-Bromo-cyclohex-2-enyl acetate, (184)



(184)

R_f ~ 0.6 (30 % Et_2O / petroleum ether) ^1H NMR (400 MHz; $CDCl_3$, 20 °C) δ: 1.65 (2H, m, C**H**$_2$), 1.88 (2H, m, C**H**$_2$), 2.10 (3H, s, CO_2**Me**), 1.95-2.25 (2H, br., m, C**H**$_2$), 5.40, (1H, t, ^3J = 4.2 Hz, C**H**OAc) 6.34 (1H, dd, ^3J = 4.8, 3.3 Hz, C**H**=CBr).

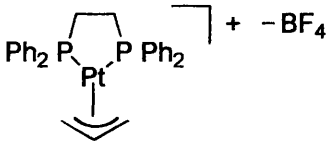
2-Bromo-1,3-diphenylpropen-2-yl acetate, (190)



(190)

R_f ~ 0.55 (30 % Et_2O / petroleum ether) ^1H NMR (400 MHz; $CDCl_3$, 20°C) δ: 2.22, 3H, s, CO_2**Me**), 6.57, 1H, s, C**H**OAc), 7.20, 1H, C**H**=CBr), 7.25-7.7, (10H, m, Ar**H**).

[(dppe)Pt(η^3-C_3H_5)]BF_4, (150)



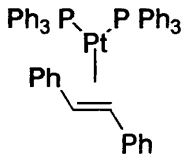
(150)

A round bottomed containing a stirring bead, $[(C_3H_5)PtCl]_4$ (0.070 g, 0.0644 mmol, 1 equiv.) and dppe (0.103 g, 0.258 mmol, 4.0 equiv.) was evacuated and then charged with THF (5 ml) and nitrogen. The resulting suspension was stirred at 40

°C for five minutes. The flask is then briefly opened and charged with $AgBF_4$ (0.050 g, 0.258 mmol, 4.0 equiv.). It was then stirred for a further five mins at 40 °C, cooled to room temperature and filtered through a pad of Celite. The Celite was washed with DCM. The resulting solution had solvent removed and was dried *in vacuo*. Yield: 0.091 g, 0.126 mmol, 49 %. As this complex was prepared on a small scale by a route which is similar to the synthesis of $[(Ph_3P)_2Pt(C_3H_5)]BF_4$,[108] it was not as fully characterised as most other compounds reported in this thesis. However, NMR and High Res. mass spec. confirm both its purity and formula. ^{31}P NMR (161.7 MHz; $CDCl_3$, 20 °C) 47.4 (^1J = 3694 Hz), ^1H NMR (400 MHz; $CDCl_3$, 20 °C)δ: 2.65, (brs, 4H, CH_2CH_2), 2.85, (sbr, 2H), 3.7 (brs, 2H), 4,7 (brs, 1H) HRMS, (F. A. B.; m/z): (M - BF_4)+ Req's: 634.1392: Found: 634.1384.

.

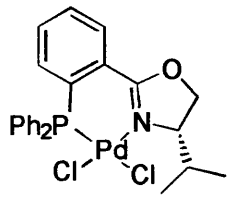
$(Ph_3P)_2Pt$-stilbene[149]



This compound was first prepared many years ago.[149] The procedure shown here is in greater detail and gives more analytical data than the original (brief) report.
To an evacuated three necked flask containing $(Ph_3P)_2PtCl_2$ (0.5 g, 0.632 mmol) and a stirring bead was added degassed ethanol (10 ml). Hydrazine hydrate was then added (0.5 ml, 0.010 mmol), and the reaction mixture, which goes clear in a few minutes, was filtered using a cannula filter into a Schlenk flask containing trans-stilbene (0.15 g, 0.833 mmol) and warmed to 60 °C - 70 °C for ten minutes. The pale yellow precipitate which was formed on cooling was filtered off (under nitrogen) and washed with ethanol (5 ml), water (5 ml) and ethanol again (5 ml). It

was then dried under high vacuum. The compound can be handled on the bench with no problems and can be stored for long periods under nitrogen. Yield: 0.250 g, 0.277 mmol, 44%. $\upsilon_{max.}$/ cm^{-1} (nujol) 1594, 1304, 1181, 1092; ^{31}P NMR (161.7 MHz; $CDCl_3$, 20 °C) 14.2 (^1J = 3676 Hz) ^1H NMR (400 MHz; $CDCl_3$, 20 °C) 6.8-7.9 (m, Ar**H**). MS. (F.A.B.+; m/z) 719 (100) (M-stilbene).

[(*S*)-P^N]$PdCl_2$, (156)

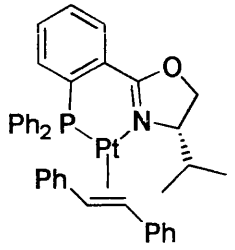


(156)

To an evacuated one-necked round bottomed flask containing $PdCl_2$ (0.057 g, 0.318 mmol) and ligand **(64)** (S)-P^N (0.113 g, 0.303 mmol) was added DCM. The flask was then flushed with nitrogen and heated to reflux for 40 hours. The brown reaction mixture was filtered before having solvent removed. The resultant yellow precipitate was washed with Et_2O and collected on filter paper. It was then dissolved, filtered and dried to yield the pure product. The compound can also be conveniently prepared from (COD)$PdCl_2$ by stirring with the ligand in DCM at room temperature. Crystals of the DCM solvate complex suitable for X-ray diffraction experiments were grown from DCM. Yield: c. 70 % for both methods. (Found: C, 47.2, H, 4.08, N, 2.16. $C_{25}H_{26}Cl_4NOPPd$ requires C, 47.2, H, 4.09, N, 2.20); m.p. = >250 °C; $\upsilon_{max.}$/ cm^{-1} (nujol) 1626, 1570, 1247, 1101.. ^{31}P NMR (161.7 MHz; $CDCl_3$, 20 °C) 26.49. ^1H NMR (400 MHz; $CDCl_3$, 20 °C) 0.01 (3H,d, ^3J =6.8 Hz, C**H**$_3$), 0.83 (3H,d, ^3J=7.2 Hz, C**H**$_3$), 2.66, (1H, m, C**H**$(CH_3)_2$),

4.37 (1H, q, CH_2O), 4.49 (1H, t, CH_2O), 5.58 (1H, m, CHN), 6.93-8.14 (14H, m, ArH). MS. (F.A.B.-; m/z) 548.9 (M+).

Attempted preparation of [(*S*)-P^N]Pt-stilbene, (151).



(151)

All procedures for this synthesis were carried out in the absence of air. To a stirred solution of [(*S*)-P^N]$PtCl_2$ (0.300 g, 0.469 mmol) and stilbene (0.085 g, 0.469 mmol) in dry THF (9 ml) was added a solution of $NaBH(OMe)_3$ (0.156 g, 1.219 mmol in 4 ml THF). This was stirred for one hour. The THF was then removed *in vacuo* and the resultant black residue redissolved in toluene and filtered through a pad of Celite™ The Celite was washed with toluene. The solvent was then removed and the residue was recrystallised by cooling a DCM / hexane solution to -70 °C to give an orange / brown powder in low to moderate yield. This impure material catalysed allylic alkylation enantioselectively. $\upsilon_{max.}$/ cm^{-1} (nujol) 1732, 1597, 1300, 1154; ^{31}P NMR (161.7 MHz; $CDCl_3$, 20 °C) 9.76 (^3J = 4453 Hz) Peaks also at 29.56 and 0.62. ^1H NMR (400 MHz; $CDCl_3$, 20 °C) 0.13 (d, ^3J = 7.0 Hz), 0.81 (d, ^3J=7.0 Hz), 2.55 (m), 3.8 (m), 4.3-4.4 (m with satellites ^2J = 104 Hz), 5.35 (m), 6.93-8.14 (m, ArH). MS. (FAB+; m/z) 659 (70), 568 (55) [M-stilbene]+, 180 (100) [stilbene]. HRMS: $C_{24}H_{24}NOPPt$ requires 568.1243, Found: 568.1224;

General procedure for allylic substitution reactions using zerovalent platinum catalysts.

To an evacuated round bottomed flask containing 5 mol% catalyst and stirring bead (and the chiral ligand, if appropriate) was added a solution of the allylic acetate in dry solvent. The flask is then flushed with nitrogen. A solution of $NaCH(CO_2Me)_2$ (1.7 equiv.) was then added, and the reactions were stirred at the desired temperature for the given time. The reactions were then diluted with DCM and washed with NH_4Cl. The aqueous layer was washed with more DCM, and the organic extracts were combined and washed with water and brine. Column chromatography using 20% ether / petroleum ether as eluent gave the desired product.

Typical procedure for allylic alkylation using [(*S*)-P^N]MCl_2 / $NaBH(OMe)_3$

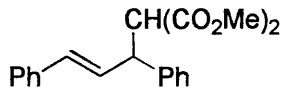
To an evacuated round bottomed flask containing stirring bead, **[(*S*)-P^N]$PtCl_2$,** (10 mg, 1.56 x 10^{-5} mols) and [(*S*)-P^N if applicable] was added dry THF (1.2 ml). The flask was then flushed with nitrogen. This was stirred for a few minutes, before the addition of a THF solution of $NaBH(OMe)_3$ (4.5 mg, 3.2 x 10^{-5}mols in 1.2 ml). After 1-2 minutes stirring, a THF solution of *rac*-(*E*)-1,3-diphenyl-prop-2-enyl acetate (80 mg, 3.18 x 10^{-4} mol) was added. A THF solution of sodium dimethyl malonate (83 mg, 5.39 x 10^{-4} mol) was then added, and the reaction was heated to the desired temperature for the appropriate time. The reaction was monitored by removing 0.1 ml of reaction mixture, filtering through a pipette containing cotton wool and a pad of silica (using ether as eluent), removing solvent, and analysing a solution of the resultant oil by HPLC (Chiracel OD®, Hex./ ^{i}PrOH:

99:1) It is possible to determine conversion, and e.e. of products and starting material using this method. When the reactions had finished they were diluted with DCM (30 ml) and washed with ammonium chloride. The aqueous layer was washed with DCM and the combined organic extracts were washed with water (50 ml), brine (40 ml), dried ($MgSO_4$) and have solvent removed. Pure product **(149)** was obtained after column chromatography using 20% ether / petroleum ether as eluent. It was identified by comparison of its ^1H and ^{13}C NMR, T.L.C. and HPLC data with that of an authentic sample.[80, 115]

Typical procedure for allylic alkylation using $[(C_3H_5)PtCl]_4$ as catalyst.

To an evacuated round bottomed flask containing stirring bead, **$[(C_3H_5)PtCl]_4$**, (4.0 mg, 3.73 x 10^{-6} mols) and (*S*)-P^N (5.3 mg, 1.43 x 10^{-5} mol) was added dry THF (1.5 ml). The flask was then flushed with nitrogen. This was stirred for a few minutes, before the addition of a THF solution of *rac*-(*E*)-1,3-diphenyl-prop-2-enyl acetate (80 mg, 3.18 x 10^{-4} mol in 1.0 ml THF). The sodium dimethylmalonate solution (78 mg, 5.3 x 10^{-4} mols) was added next. The reaction was then stirred at the desired temperature and worked up and purified as before.

Methyl 2-methoxycarbonyl-3,5-diphenyl penten-1-oate, (149)

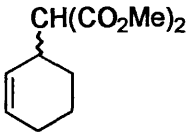


(149)

R_f**(149)** ~ 0.35, (30 % Et_2O / Petrol); $\upsilon_{max.}/cm^{-1}$ (neat) 1730, 1598, 1493, 1248, 1218, 1156 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 20 °C): 3.53 (3H, s, CO_2CH_3), 3.72

(3H, s, $CO_2C\mathbf{H}_3$), 3.97 (1H, d, ^3J=11.0 Hz, $\mathbf{H}C(CO_2Me)_2$), 4.29 (1H, dd, ^3J=11.0, 8.4 Hz, C**H**CH), 6.34 (1H, dd, ^3J=15.8, 8.3 Hz, =C**H**), 6.50 (1H, d, ^3J=15.9 Hz, =C**H**), 7.20-7.35 (10H, m, Ar**H**). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ: 49.06 (**C**H), 52.25 ($\mathbf{C}H_3$), 52.43 ($\mathbf{C}H_3$), 57.47 (**C**H), 126.22, 127.02, 127.42, 127.73, 128.57, 128.99: (Ar**C**= and **C**=**C**), 131.67 (Ar**C**), 136.68 (Ar**C**), 167.61, (**C**=O), 168.03 (**C**=O).. MS (EI; m/z) 324 (10), 205 (80), 193 (60), 149 (80), 101 (100). $C_{20}H_{20}O_4$ requires: 324.1361, Found: 324.1362

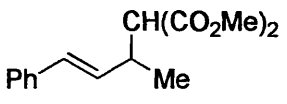
Methyl-2-carbomethoxy-2-cyclohexenyl ethanoate, (160)



(160)

R_f**(160)** ~ 0.75; R_f**(159)** ~ 0.9; (30 % Et_2O / petrol); $\upsilon_{max.}$/ cm^{-1} (thin film) 2932, 1736, 1649, 1435, 1332, 1267, 1195, 1160; ^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): 1.4-1.9 (4H, m, $C\mathbf{H}_2C\mathbf{H}_2$), 2.00 (2H, m, $C\mathbf{H}_2$), 2.92 (1H, m, C**H**CH), 3.30 (1H,d, ^3J=9.5 Hz, $\mathbf{H}C(CO_2Me)_2$), 3.74 (s, 3H, $CO_2\mathbf{Me}$), 3.75 (s, 3H, $CO_2\mathbf{Me}$), 5.54 (m, 1H, =C**H**), 5.79, (1H, m, C**H**=). ^{13}C NMR (67.9 MHz, $CDCl_3$) 20.77 (CH_2), 24.83 (CH_2), 26.52 (CH_2), 35.29 (CH), 52.27 (CH), 127.23 (=CH), 129.55 (HC=), 168.74, (C=O), 168.79 (C=O). MS. (EI; m/z) 212 (10) [M+], 152 (100), 93 (25), 81 (50). $C_{11}H_{16}O_4$ req's: 212.1048, Found: 212.1044

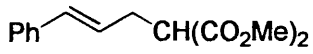
Methyl-2-carbomethoxy-3-methyl-5-phenyl pent-4-enoate, (195)



(195)

R_f**(195)** ~ 0.4; R_f**(194)** ~ 0.55; (30 % Et_2O / petrol); $\upsilon_{max.}$ cm^{-1} (thin film) 3026, 2953, 1738, 1598, 1578, 1494, 1435, 1246, 1194, 1158, 1023, 969; ^1H NMR (270 MHz, $CDCl_3$, 20 °C): 1.10 (3H, d, ^3J = 6.8Hz, CHC**H**$_3$), 3.0-3.1 (1H, m, C**H** CH_3), 3.23 (1H, d, ^3J = 7.9 Hz, CHC**H**), 3.58 (1H, s, CO_2**Me**), 3.61 (1H, s, CO_2**Me**), 6.04, (1H, dd, ^3J = 8.4, 15.8, =C**H**), 6.36 (1H, d, ^3J = 15.9 Hz, =C**H**), 7.1 (5H, m, Ar**H**). ^{13}C NMR (67.9 MHz, $CDCl_3$): 18.37 (CH_3), 37.62 (CH), 52.22 (CH_3), 52.30 (CH_3), 57.70 (CH), 126.16, 127.28, 127.65, 128.39, 130.71, 131.09 (ArCH & =CH), 137.0 (ArC-), 168.50 (C=O). MS. (E. I. m/z) 262 (10) [M+], 202 (20), 143 (55), 131 (100). $C_{15}H_{18}O_4$ requires: 262.1205, Found: 262.1201.

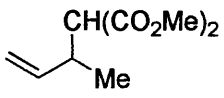
Methyl-2-methoxycarbonyl-5-phenyl-4-pentenoate, (130)



(130)

R_f**(130)** ~ 0.3; R_f**(193, S.M.)** ~ 0.4; (20 % Et_2O / petrol); $\upsilon_{max.}$/ cm^{-1} 1745, 1682, 1149, 1047, 1006, 964; ^1H NMR (270 MHz, $CDCl_3$, 20 °C): 2.80 (2H, dt, (app), ^3J = 7.3, 1.2 Hz, =CHC**H**$_2$), 3.55 (1H, t, ^3J = 7.3 Hz, CH_2C**H**), 3.75 (3H, s, CO_2**Me**), 3.76 (3H, s, CO_2**Me**), 6.1 (1H, dt, ^3J = 7.3, 15.6 Hz, =C**H**), 6.47 (1H, d, ^3J = 15.6 Hz, =C**H**), 7.2-74 (5H, m, Ar**H**). MS. (EI; m/z) 248 (25), 188 (35), 129 (80), 117 (55). $C_{14}H_{16}O_4$ requires: 248.1049, Found: 248.1046.

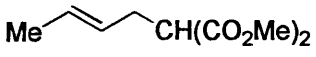
Methyl-2-methoxycarbonyl-3-methyl-4-pentenoate, (126)



(126)

R_f**(126)** ~ 0.6; R_f**(125, S. M.)** ~ 0.8; (30 % Et_2O / petrol); $\upsilon_{max.}$/ cm^{-1} (thin film) 2956, 1737, 1644, 1566, 1436, 1268, 1199, 1154; ^1H NMR (270 MHz, $CDCl_3$, 20 °C): 1.03 (3H, d, ^3J = 6.8 Hz, CHC**H**$_3$), 2.89 (1H, hex (app) C**H**Me), 3.24 (1H, d, ^3J = 9.0 Hz, C**H**CH), 3.66 (3H, s, CO_2**Me**), 3.67 (3H, s, CO_2**Me**), 4.99 (2H, ddm, =C**H**$_2$), 5.70 (1H, ddd, =C**H**). ^{13}C NMR (67.9 MHz, $CDCl_3$): 18.38 (CH_3), 38.51 (CH), 52.69 (CH_3), 52.78 (CH_3), 57.89 (CH), 115.76 (CH_2), 139.80 (CH), 168.75 (CO_2Me), 168.81 (CO_2Me).

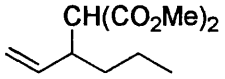
Methyl-(E)-2-methoxycarbonyl-4-hexenoate, (127)



(127)

^1H NMR (270 MHz, $CDCl_3$, 20 °C): 1.56 (3H, dd, C**H**$_3$CH), 2.50 (2H,dd, ^3J = 6.7, 7.5 Hz, CHC**H**$_2$), 3.34 (1H, t, ^3J = 7.7Hz, CH_2C**H**), 3.64 (6H, s, CO_2Me), 5.30 (1H, m, =C**H**), 5.49 (1H, m, =C**H**). ^{13}C NMR (67.9 MHz, $CDCl_3$): 30.11 (CH_3), 32.31 (CH), 38.51 (CH), 52.32 (CH_3), 126.47 (=CH), 128.76 (=CH), 169.57 (CO_2Me).

Methyl-3-ethenyl-2-methoxycarbonylhexanoate, (198)

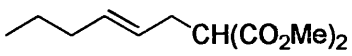


(198)

R_f**(198)** ~ 0.3; R_f**(197, S.M.)** ~ 0.7; (10 % Et_2O / pet. ether); $\upsilon_{max.}$/ cm^{-1} (thin film) 2956, 1739, 1641, 1436, 1256, 1195, 1147; ^1H NMR (270 MHz, $CDCl_3$, 20 °C): 0.80 (3H, t, ^3J = 7.1 Hz, C**H**$_3$CH$_2$), 1.1-1.4 (4H, m, C**H**$_2$C**H**$_2$), 2.70 (1H, dq (app), CH_2C**H**), 3.31 (1H, d, ^3J = 9.0 Hz, CHC**H**), 3.62 (3H, s, CO_2Me), 3.66 (3H, s, CO_2Me), 4.98 (1H, s (app.), =C**H**H), 5.03 (1H, dm, =CH**H**), 5.55 (1H, dt (app), ^3J = 9.4, 18 Hz). ^{13}C NMR (67.9 MHz, $CDCl_3$): 13.75 (CH_3), 20.09 (CH_2), 34.41 (CH_2),

43.98 (CH), 52.17 (CH_3), 52.33 (CH_3), 56.89 (CH), 117.32 (=CH_2), 138.04 (=CH), 168.56 (CO_2Me), 168.76 (CO_2Me). MS. (EI; m/z) 214 (15) [M+], 171 (35), 155 (100), 132 (95), 111 (60).

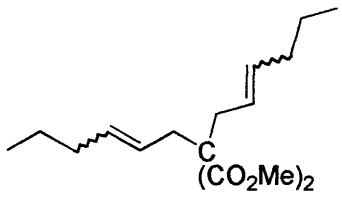
Methyl (*E*)-2-methoxycarbonyl-4-octenoate, (199)



(199)

^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): 0.84 (3H, t, ^3J = 7.3 Hz, C**H**$_3$CH$_2$), 1.33 (2H, hex. app.), CH$_3$C**H**$_2$), 1.93 (2H, q app., ^3J = 7.1 Hz), 2.56 (2H, t.(app. With fine splitting), CHC**H**$_2$), 3.40 (1H, t, ^3J = 7.3 Hz), 3.71 (6H, s, CO_2**Me**), 5.32 (1H, m, =C**H**), 5.50 (1H, m, **H**C=). ^{13}C NMR (67.9 MHz, $CDCl_3$): 13.94 (CH_3), 22.83 (CH_2), 32.34 (CH_2), 34.90 (CH_2), 52.36 (CH_3), 52.76 (CH), 125.40 (=CH), 134.14 (HC=), 169.53 (CO_2Me), 169.57 (CO_2Me). The Z-alkene, which was only present as a minor (inseparable) product, is distinguished by the following different signals in the ^{1}H NMR: 2.01 (q.app., 2H, ^3J = 7.5Hz), 2.64 (tm, 2H), 3.45 (t, 1H, ^3J = 7.6Hz)

7-Dimethoxycarbonyl-trideca-4,5-diene, (200)



(200)

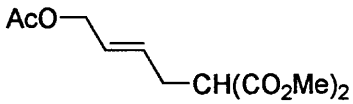
Compound **(200)** was sometimes observed (on the T.L.C plate) as a side product in the allylic alkylations on hex-2-enyl acetate. On one occasion we isolated a small amount (c. 4 mgs) of pure **(200)** and this can be assigned the structure shown by ^{1}H

NMR and mass spec. R_f**(200)** ~ 0.35; (10 % Et_2O / petrol). ^1H NMR (270 MHz, $CDCl_3$, 20 °C): 0.87 (6H, t, ^3J = 7.3 Hz, CH_2CH_3), 1.33 (4H, hex.app., CH_2CH_3) 1.95 (4H, dd, ^3J = 7.0 Hz, CH_2CH_2CH=), 2.56 (4H, d, ^3J = 6.7 Hz, CH_2CH=), 3.69 (s, 6H, $(CO_2Me)_2$), 5.22 (2H, m, =CH), 5.48 (2H, m, =CH). MS. (CI+; m/z) 297.1 (100, MH+), 236 (20), 213 (70), 181 (80).

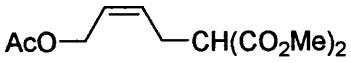
Typical procedure for allylic alkylation of *cis*-1,4-diacetoxy-2-butene using $[(C_3H_5)PdCl]_2$ and a monodentate phosphine ligand as catalyst.

To an evacuated round bottomed flask containing stirring bead, $[(C_3H_5)PdCl]_2$, (12.0 mg, 3.28 x 10^{-5} mols, 2.5 mol%) and Cy_3P (36.8 mg, 1.31 x 10^{-4} mol, 10 mol %) was added dry THF (1.5 ml). The flask was then flushed with nitrogen. This was stirred for a few minutes, before the addition of *cis*-1,4-diacetoxy-2-butene (0.210 ml, 216 mg, 13.12 x 10^{-4} mol) and the sodium dimethylmalonate solution (13.52 x 10^{-4} mols, 4.2 ml of 0.328 mmolml^{-1} soln in THF, 1.02 equiv.). The reaction was then stirred at the desired temperature until conversion was complete as judged by T.L.C.. Solvent was then removed. The ratio of branched to linear products and E /Z isomers was determined by G.C. and by crude NMR of the reaction mixture. When Cy_3P was used as ligand, it was just possible to separate the branched (major) product from the linear one by careful chromatography using 20% Et_2O / hexane as eluent. The linear product is a mixture of *cis* and *trans* isomers which are inseparable by simple methods.

(*E*) and (*Z*) Methyl 6-acetoxy-2-(methoxycarbonyl)-hex-4-enoate, (206)



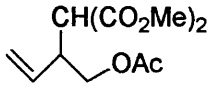
***E*-(206)**



Z-(206)

R_f**(206)** ~ 0.35; R_f**(204)** ~ 0.5; (30 % Et_2O / petrol); $\upsilon_{max.}$/ cm^{-1} (neat) 3634, 3466, 2956, 1729, 1437, 1366, 2344, 1240, 1158, 1028. ^1H NMR (270 MHz, $CDCl_3$, 20 °C): 2.03 (3H, s, C(=O)C**H**$_3$-*trans*), 2.04 (3H, s, C(=O)C**H**$_3$-*cis*), 2.63 (2H, t, app., ^3J = 6.5 Hz, =CHC**H**$_2$-*trans*), 2.69 (2H, t,app., ^3J = 7.2 Hz-*cis*), 3.44 (1H, m, CH_2C**H**-*cis* and *trans*), 3.72 (6H, s, CH(CO_2**Me**)$_2$-*trans*), 3.73 (6H, s, CH(CO_2**Me**)$_2$-*cis*), 4.47 (2H, d, ^3J = 5.0Hz, AcOC**H**$_2$-*trans*), 4.62 (2H,d, ^3J = 6.4 Hz, AcOC**H**$_2$-*cis*), 5.55-5.75 (2H, m, C**H**=C**H**-*cis* and *trans*). ^{13}C NMR (67.9 MHz, $CDCl_3$): 21.36 (CH_3-*cis* and *trans*), 27.32 (CH_2-*cis*), 31.82 (CH_2-*trans*), 51.64 (CH-*cis* and *trans*), 52.94 (CH_3-*trans*), 53.00 (CH_3-*cis*), 60.35 (CH_2-*cis*), 64.81 (CH_2-*trans*), 126.97 (=CH-*cis*), 127.47 (=CH-*trans*), 129.77 (=CH-*cis*), 130.85 (=CH-*trans*), 169.16 ($CO_2Me)_2$-*trans*), 169.20 ($CO_2Me)_2$-*cis*), 170.79 (CH_3CO_2R-*cis*), 170.93 (CH_3CO_2R-*trans*). MS. (C.I.+; m/z) 245(10) [MH+], 185 (100), 171 (10).

Methyl-3-acetoxymethyl-2-methoxycarbonylpent-4-enoate, (205)

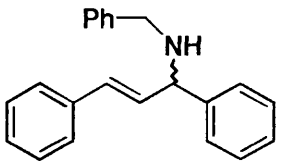


(205)

R_f**(205)** ~ 0.3; R_f**(204)** ~ 0.5; (30 % Et_2O / petrol); $\upsilon_{max.}$/ cm^{-1} (neat) 3640, 3469, 3083, 2956, 1739, 1643, 1436, 1224, 1040, 931. ^1H NMR (270 MHz, $CDCl_3$, 20 °C): 2.00 (3H, s, C(=O)C**H**$_3$), 3.13 (1H, m, =CHC**H**CH), 3.54 (1H, d, ^3J = 8.2 Hz, =CHCHC**H**), 3.68 (3H, s, CO_2C**H**$_3$), 3.71 (3H, s, CO_2C**H**$_3$), 4.07 (1H, dd, ^3J = 11.3, 6.0 Hz, HC**H**OAc), 4.20 (1H, dd, ^3J = 11.1, 5.9 Hz, **H**CHOAc), 5.14 (2H, tm [app.],

$\mathbf{H_2}$C=), 5.75 (1H, ddd, ^{3}J = 8.8, 10.2, 17.3 Hz, H_2C=C**H**). ^{13}C NMR (67.9 MHz, $CDCl_3$): 21.18 (CH_3), 43.130 (CH), 52.83 (CH_3), 52.97 (CH_3), 53.40 (CH), 65.00 (CH_2), 119.16 (=CH_2), 134.46 (=CH), 168.15 (**C**O_2Me), 168.31 (**C**O_2Me), 170.69 (O**C**(=O)Me). MS. (F.A.B.+; m/z) 267 (15), 245(50) [MH+], 185 (100), 171 (10). $C_{10}H_{17}O_6$, (MH^+) requires 245.1025, Found: 245.1015

(*E*)-N-Benzyl-(1,3-diphenyl-3-propenyl)amine, (157) [113]

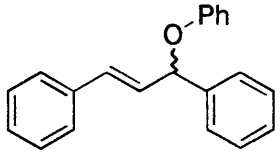


(157)

To an evacuated round-bottomed flask containing $(Ph_3P)_2$P-*trans*-stilbene (0.013 g, 1.44 x 10^{-5} mols) and a stirring bead was added a solution of diphenyl prop-2-enyl acetate (0.073 g, 2.89 x 10^{-4} mols in 3 ml THF). The flask was then flushed with nitrogen. The benzylamine (0.047 ml, 0.046 g, 4.34 x 10^{-4} mols) was then added, and the reaction stirred for 19 hours at room temperature. The reaction was then diluted with DCM and washed with ammonium chloride solution. The aqueous layer was washed with DCM, and the combined organic layers were washed with water, dried ($MgSO_4$) and had solvent removed. Drying *in vacuo* yields **(157)** (0.08 g, 2.77 x 10^{-4} mol, 96 %) which was essentially pure as determined by T.L.C. and NMR. It was identified by comparison with literature values.[113] $\upsilon_{max.}$/ cm^{-1} (thin film): 4051, 3081, 3059, 3025, 1949, 1877, 1808, 1670, 1600, 1493, 1452. ^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): 3.68 (1H, s, **H**CHN), 3.69 (1H, s, **H**CHN), 4.30 (1H, d, ^{3}J = 7.5 Hz, C**H**N), 6.22 (1H, dd, ^{3}J = 15.8, 8.8 Hz, =C**H**), 6.49 (1H, d, ^{3}J = 15.9Hz, HC=), 7.01-7.43 (15H, m, Ar**H**). ^{13}C NMR (67.9 MHz, $CDCl_3$, 20 °C)

51.33 (NCH_2), 64.55 (CHN), 126.38-128.59 (ArH), 130.37 (=CH), 132.50 (CH=), 136.89 (ArC-), 140.28 (ArC-), 142.78 (ArC-); MS. (EI +; m/z): 299.2 (10) [M^+], 208 (35), 180.1 (100), 149 (70). $C_{22}H_{21}N$ (M+) requires: 299.1674; Found: 299.1668.

(*E*)-1,3-Diphenyl-prop-2-enol phenyl ether, (158).[114]

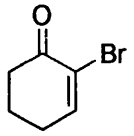


(158)

To an evacuated round-bottomed flask containing $(Ph_3P)_2P$-ethylene (0.022 g, 2.9×10^{-5} mols) and a stirring bead was added a solution of diphenyl prop-2-enyl acetate (0.147 g, 5.80×10^{-4} mols in 2 ml DCM). The KF on Alumina (0.260 g, 1.8 mmol, 2 equiv) was then poured into the reaction vessel. The flask was then flushed with nitrogen, before the addition of a solution of phenol (0.083 g, 8.75×10^{-4} mols in 2 ml DCM). The reaction was stirred for 60 hours at room temperature. The reaction was then diluted with DCM and washed with ammonium chloride solution. The aqueous layer was washed with DCM, and the combined organic layers were washed with water, dried ($MgSO_4$) and had solvent removed. Purification by column chromatography on silica using 10% Et_2O / petroleum ether as eluent gives **(158)** Yield: (0.107 g, 3.77×10^{-4} mol, 65 %) It was identified by comparison of its T.L.C., HPLC, and ^1H NMR data with an analytically pure sample kindly provided by another group member.[114] $R_f \sim 0.7$ (20 % Et_2O / pet. ether, U.V.); ^1H NMR (270 MHz, $CDCl_3$), 20 °C) δ: 5.79 (1H, d, ^3J =

7.0 Hz, CHOPh), 6.43 (1H, dd, ^3J = 16.0, 7.0 Hz, =CHCH), 6.66 (1H, dd, ^3J = 16 Hz, PhCH), 6.88-6.99 (3H, m, ArH), 7.18-7.47 (12H, m, ArH).

2-Bromo-cyclohex-2-en-1-one, (183)[128]

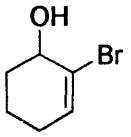


(183)

The preparation of this compound from 2-cyclohexenone has previously been described by Kowalski *et. al.*[128, 129] A solution of bromine (1.06 ml, 20.64 mmol in 10 ml DCM) was slowly added to a cooled (0 °C) solution of 2-cyclohexenone (2.0 ml, 1.986 g, 20.7 mmol in 50 ml DCM). This solution was stirred at 0 °C for an hour before the dropwise addition of triethylamine (4.6 ml, 33 mmol). The solution was then stirred for 90 minutes. It was washed with 3% HCl (2 x 20 ml) and brine (1 x 30 ml). The organic layer was then dried and had all solvent evaporated to give an oil. This was recrystallised by dissolving in the minimum volume of ethyl acetate and layering with hexane until the first signs of precipitation appear. It was then left in the fridge overnight to give white crystals. (yield 1.384 g, 7.91 mmol, 38 %) These were filtered off and washed with hexane. A second crop of crystals can be obtained from the filtrate by repeating the recrystallisation process (Yield: 0.814 g, 4.65 mmol, 23 %). The overall yield is 61 %. Both crops of crystals give very clean NMR spectra. $R_f \sim 0.25$; $\upsilon_{max.}$/ cm^{-1} (nujol) 1704, 1680, 1596, 1315, 1158, 1124, 1070. ^1H NMR (270 MHz, $CDCl_3$), 20 °C) δ: 2.05 (2H, qn app., CH_2CH=), 2.42 (2H, m, CH_2CH_2CH=), 2.60 (2H, m, CH_2C=O), 7.41 (1H, t, ^3J = 4.4 Hz, BrC=CH). ^{13}C NMR (67.9 MHz, $CDCl_3$, 20 °C)δ: 22.57 (CH_2), 28.28

(CH_2), 38.26 (CH_2), 123.74 (=CBr), 151.16 (=CH), 191.16 (C=O). m.p. = 74-78 °C (Lit. 75-76 °C);[128, 129] MS. (EI +; m/z) 176 (70), 174 (70, M+), 148 (90), 146 (90), 120 (30), 118 (30). C_6H_7OBr requires 173.9680. Found, 173.9678.

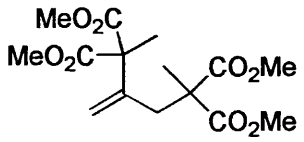
2-bromo-cyclohex-2-en-1-ol, (184)



(184)

Cerium chloride heptahydrate, (2.12 g, 5.71 mmol, 1.0 equiv.), 2-bromo-cyclohex-2-en-1-one, (1.0 g, 5.71 mmol, 1 equiv.) were dissolved in methanol (20 ml) and cooled to 0 °C. Sodium borohydride, $NaBH_4$, (0.260 g, 6.856 mmol, 1.2 equiv.) was then added portionwise over about 20 minutes. The reaction was then stirred for another two hours. There is no change in R_f in going from starting material to product. The reaction mixture was diluted with diethyl ether (50 ml) and washed with water (50 ml). The aqueous layer was then washed twice with Et_2O (40 ml). The organic extracts were combined and washed with water (80 ml), dried ($MgSO_4$) and had solvent removed to give a colourless oil. This oil crystallised after drying under high vacuum. This crude product showed no impurities in its NMR spectrum. (yield: 0.831 g, 4.69 mmol, 82%) R_f = 0.25 (30% Et_2O / petrol); m.p. = 37 °C; $\upsilon_{max.}$/ cm^{-1} (nujol) 3597, 1640, 1307, 1165, 1053, 979 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$), 1.5-2.1 (6H, m, $\mathbf{CH_2CH_2CH_2}$), 2.31 (1H, br, d-app., O-**H**), 4.15 (1H, br, d-app., C**H**OH), 6.14 (1H, t, ^3J = 4.2 Hz, $CH_2C\mathbf{H}$=). ^{13}C NMR (67.9 MHz, $CDCl_3$, 20 °C): 17.55 (CH_2), 27.73 (CH_2), 31.93 (CH_2), 69.77 (CHO), 125.72 (=CBr), 132.50 (=CH). MS. (EI+; m/z) 178 (30), 176 (30,M+), 150 (15), 148 (15), 97 (100). C_6H_9OBr requires: 175.9837, Found: 175.9839.

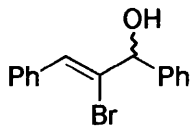
Methyl 2-methoxycarbonyl-2-methyl-3-vinylene-5-methoxycarbonyl)-5-methylhexan-1,6-dioate, (179)



(179)

To an evacuated round bottomed flask containing $(Ph_3P)_2$-*trans*-stilbene (20 mg, 0.022 mmol, 5 mol%) and a stirring bead was added a solution of the 2-chloro allyl acetate (0.060 g, 0.44 mmol, 1 equiv. in dry THF). The flask was then flushed with nitrogen. A solution of $NaC(Me)(CO_2Me)_2$ (1.55 mmol, 3.5 equiv.) was then added, and the reaction was stirred at the room temperature for 48 hours. The reactions were then diluted with DCM and washed with NH_4Cl. The aqueous layer was washed with more DCM, and the organic extracts were combined and washed with water and brine. Column chromatography using 30% ether / petroleum ether ($R_f \sim 0.25$) as eluent gave the desired product. Yield: 0.075g, 0.23 mmol, 52 %. $\upsilon_{max.}$/ cm^{-1} (neat) 3001, 2955, 2095, 1732, 1645, 1435, 1379, 1252, 1110, 985 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ: 1.42 (3H, s, ($CC\mathbf{H_3}$), 1.54 (3H, s, ($CC\mathbf{H_3}$), 2.76 (2H, s, $CC\mathbf{H_2}C$), 3.66 (6H, s, ($CO_2\mathbf{Me}$), 3.68, (6H, s, $CO_2\mathbf{Me}$), 4.84 (1H, d, ^3J = 1.4 Hz, **H**HC=), 4.98 (1H, d, ^3J = 1.3 Hz, H**H**C=). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ: 19.14, (CH_3), 20.81 (CH_3), 36.86 (CH_2), 52.61 (CH_3), 52.67 (CH_3), 53.03, (R_4C), 61.12 (R_4C), 114.2 (=CH_2), 141.35 (R_4C), 171.2 (C=O), 172.67 (C=O). MS (F.A.B.+; m/z) 331 (100, MH+). 271 (35), 239 (10), 179 (10). $C_{15}H_{23}O_8$, (MH+) requires: 331.1392, Found: 331.1392.

2-bromo-1,3-diphenylprop-2-en-3-ol, (189)



(189)

A solution of α-bromo-cinnamaldehyde (1.0 g, 4.74 mmol) in dry THF (24 ml) was cooled to 0 °C. An excess of phenyl magnesium bromide was then added *via* a syringe (between 5 and 8 mmol) and the reaction was stirred under nitrogen for two hours. Ammonium chloride was then added carefully (50 ml) and the resultant mixture poured into DCM. The organic layer was separated and washed with brine (40 ml), dried ($MgSO_4$) and had its solvent removed *in vacuo*. Column chromatography using 25% Et_2O / petroleum ether (R_f **(189)** ~ 0.45, R_f (S.M.) ~ 0.5) gave the desired alcohol, **(189)**. Yield, 1.183 g, 4.09 mmol, 86%. $\upsilon_{max.}$/ cm^{-1} (neat) 3662, 3027, 1952, 1639, 1596, 1492, 1448, 1261, 1189. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.70, s, br, 1H, (O**H**), 5.47, d, 1H, ^3J = 5.0 Hz, (C**H**OH), 7.23-7.70 m, 11H, (ArH & **H**C=). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ: 79.49 (CH), 115.5 (=CBr), 126.96 (HC=), 128.42-129.39 (ArCH), 135.15 (Ar**C**-C=), 140.59 (Ar**C**-CH(R)OH). MS. (EI+; m/z) 288 (15, M+), 209 (95), 191 (40), 170 (30), 94 (100). $C_{15}H_{13}OBr$ requires 288.0150, Found: 288.0151.

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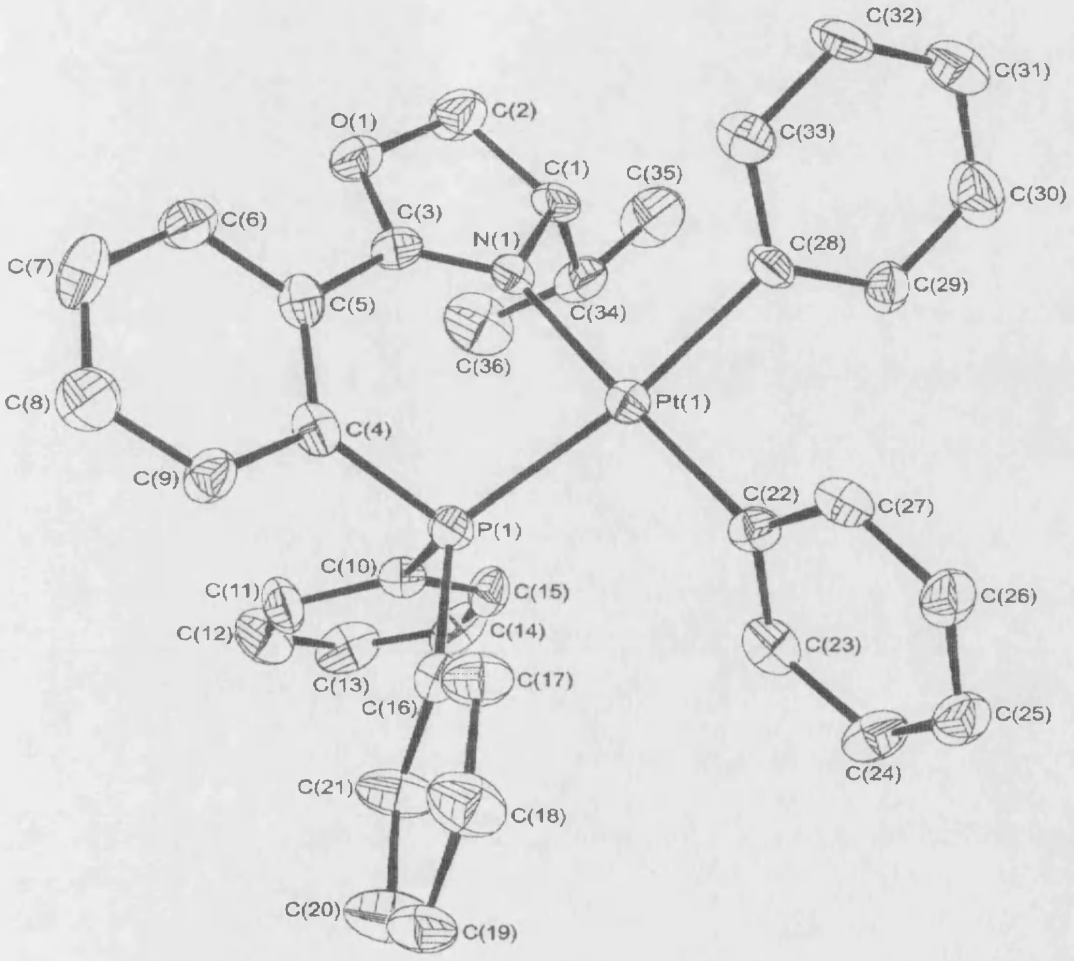
Appendix 1

Crystallographic data

All crystal structure determinations were kindly performed by

Dr. Mary F. Mahon.

X-Ray crystal structure determination of [(S)-P^N] $PtPh_2$, (75)



A crystal of approximate dimensions 0.25 x 0.25 x 0.2 mm was used for data collection.

Crystal data: $C_{36}H_{34}NOPPt$, M = 722.70, Monoclinic , a = 9.388(1), b = 16.113(2), c = 10.045(1) Å , b = 90.31(1)°, U = 1519.5(3) Å^3, space group $P2_1$, Z = 2, D_c = 1.580 gcm^{-3}, m(Mo-K_a) = 4.699 mm^{-1}, F(000) = 716. Crystallographic measurements were made at 293(2)° K on a CAD4 automatic four-circle diffractometer in the range 2.02<q<23.92°. Data (2486 reflections) were corrected for Lorentz and polarization and also for absorption.[150] (Max. and Min absorption corrections; 1.00, 0.496 respectively). In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant. The solution of the structure (SHELX86)[151] and refinement (SHELX93)[152] converged to a conventional [i.e. based on 2099 F^2 data with Fo>4s(Fo)] $R1$ = 0.0326 and $wR2$ = 0.0690. Goodness of fit = 1.016. The max. and min. residual densities were 1.133 and -1.058 eÅ^{-3} respectively. The asymmetric unit (shown in Fig. 2.17), along with the labelling scheme used was produced using ORTEX.[60]

Table 6.1. Crystal data and structure refinement for [(S)-P^N] $PtPh_2$, (75)

Empirical formula	$C_{36}H_{34}NOPPt$	Index ranges	-10<=h<=10; 0<=k<=18; 0<=l<=11
Formula weight	722.70	Reflections collected	2486
Temperature	293(2)°K	Independent reflections	2486 [R(int) = 0.0000]
Wavelength	0.70930 Å	Absorption correction	DIFABS
Crystal system	Monoclinic	Max. and min. transmission	1.00 and 0.496
Space group	$P2_1$	Refinement method	Full-matrix least-squares on F^2
Unit cell dimensions	a = 9.388(1)Å	Data / restraints / parameters	2486 / 1 / 365
	b = 16.113(2)Å b = 90.31(1)° c = 10.045(1)Å	Goodness-of-fit on F^2	1.016
		Final R indices [I>2s(I)]	R1 = 0.0326 wR2 = 0.0690
Volume	1519.5(3) Å^3	R indices (all data)	R1 = 0.0486 wR2 = 0.0757
Z	2	Absolute structure parameter	0.01(2)
Density (calculated)	1.580 Mg/m^3	Largest diff. peak and hole	1.133 and -1.058 eÅ^{-3}
Absorption coefficient	4.699 mm^{-1}	Weighting scheme	calc w=1/[σ^2(Fo^2)+(0.0462P)^2+0.0000P] where P=(Fo^2+2Fc^2)/3
F(000)	716	Extinction coefficient	0.0000(3)
Crystal size	0.25 x 0.25 x 0.2 mm	Extinction expression	Fc*=kFc[1+0.001xFc^{2}l^3/sin(2q)]$^{-1/4}$
Theta range for data collection	2.02 to 23.92 °.		

Table 6. 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for (75). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Pt(1)	1781(1)	-11(1)	253(1)	37(1)
P(1)	2664(4)	-536(2)	-1693(3)	39(1)
N(1)	450(11)	705(8)	-958(10)	45(3)
O(1)	-1047(10)	1104(7)	-2594(10)	58(3)
C(1)	70(14)	1583(9)	-640(14)	51(4)
C(2)	-1127(18)	1766(12)	-1623(18)	73(5)
C(3)	-161(13)	517(9)	-2083(15)	41(3)
C(4)	1134(14)	-792(9)	-2722(13)	43(3)
C(5)	-71(16)	-263(8)	-2832(16)	43(4)
C(6)	-1218(16)	-448(10)	-3707(16)	58(4)
C(7)	-1166(19)	-1168(11)	-4440(16)	67(5)
C(8)	-45(18)	-1690(10)	-4372(18)	68(4)
C(9)	1087(15)	-1490(9)	-3504(14)	51(3)
C(10)	3673(11)	181(7)	-2731(11)	34(4)
C(11)	3749(13)	56(25)	-4103(11)	60(4)
C(12)	4573(18)	674(11)	-4815(16)	68(5)
C(13)	5305(17)	1262(10)	-4210(20)	67(5)
C(14)	5271(21)	1315(15)	-2825(22)	68(6)
C(15)	4445(15)	797(8)	-2085(13)	47(3)
C(16)	3721(13)	-1485(9)	-1719(12)	42(3)
C(17)	3276(16)	-2147(10)	-972(16)	58(4)
C(18)	3998(19)	-2905(11)	-971(18)	71(5)
C(19)	5282(18)	-2950(11)	-1658(17)	66(5)
C(20)	5763(19)	-2291(12)	-2352(22)	83(6)
C(21)	4981(22)	-1556(13)	-2399(25)	68(7)
C(22)	3072(14)	-642(8)	1485(13)	39(3)
C(23)	4550(16)	-561(9)	1404(15)	52(4)
C(24)	5450(17)	-952(10)	2370(17)	58(4)
C(25)	4912(16)	-1448(10)	3327(15)	55(4)
C(26)	3462(16)	-1542(9)	3418(14)	52(4)
C(27)	2567(14)	-1125(9)	2530(13)	45(3)
C(28)	707(14)	432(9)	1876(12)	44(3)
C(29)	1340(15)	821(9)	2963(12)	46(3)
C(30)	559(20)	1105(12)	4018(16)	74(5)
C(31)	-917(18)	1071(10)	4019(17)	65(4)
C(32)	-1573(16)	677(11)	2970(15)	62(4)
C(33)	-807(15)	359(10)	1885(14)	58(4)
C(34)	1330(16)	2158(10)	-757(16)	58(4)
C(35)	1054(24)	2998(13)	-37(24)	95(7)
C(36)	1786(25)	2313(14)	-2176(22)	97(7)

Table 6.3. Bond lengths [Å] and angles [°] for (75).

Pt(1)-C(22)	2.006(13)	C(10)-P(1)-Pt(1)	116.5(4)
Pt(1)-C(28)	2.050(12)	C(3)-N(1)-C(1)	107.6(12)
Pt(1)-N(1)	2.086(11)	C(3)-N(1)-Pt(1)	129.6(10)
Pt(1)-P(1)	2.289(3)	C(1)-N(1)-Pt(1)	122.8(8)
P(1)-C(4)	1.813(14)	C(3)-O(1)-C(2)	107.0(11)
P(1)-C(16)	1.824(14)	N(1)-C(1)-C(34)	112.2(11)
P(1)-C(10)	1.825(11)	N(1)-C(1)-C(2)	102.8(12)
N(1)-C(3)	1.30(2)	C(34)-C(1)-C(2)	114.0(14)
N(1)-C(1)	1.49(2)	O(1)-C(2)-C(1)	104.7(12)
O(1)-C(3)	1.36(2)	N(1)-C(3)-O(1)	115.6(13)
O(1)-C(2)	1.45(2)	N(1)-C(3)-C(5)	128.3(13)
C(1)-C(34)	1.51(2)	O(1)-C(3)-C(5)	116.1(12)
C(1)-C(2)	1.52(2)	C(9)-C(4)-C(5)	115.1(13)
C(3)-C(5)	1.47(2)	C(9)-C(4)-P(1)	122.4(11)
C(4)-C(9)	1.37(2)	C(5)-C(4)-P(1)	122.4(10)
C(4)-C(5)	1.42(2)	C(4)-C(5)-C(6)	121.6(12)
C(5)-C(6)	1.42(2)	C(4)-C(5)-C(3)	121.4(13)
C(6)-C(7)	1.37(2)	C(6)-C(5)-C(3)	116.9(13)
C(7)-C(8)	1.35(2)	C(7)-C(6)-C(5)	118.7(14)
C(8)-C(9)	1.41(2)	C(8)-C(7)-C(6)	122(2)
C(10)-C(15)	1.39(2)	C(7)-C(8)-C(9)	118(2)
C(10)-C(11)	1.39(2)	C(4)-C(9)-C(8)	124.3(14)
C(11)-C(12)	1.45(3)	C(15)-C(10)-C(11)	122(2)
C(12)-C(13)	1.32(2)	C(15)-C(10)-P(1)	117.1(9)
C(13)-C(14)	1.39(3)	C(11)-C(10)-P(1)	120(2)
C(14)-C(15)	1.36(3)	C(10)-C(11)-C(12)	115(2)
C(16)-C(17)	1.37(2)	C(13)-C(12)-C(11)	123(2)
C(16)-C(21)	1.37(2)	C(12)-C(13)-C(14)	119(2)
C(17)-C(18)	1.40(2)	C(15)-C(14)-C(13)	122(2)
C(18)-C(19)	1.39(2)	C(14)-C(15)-C(10)	119(2)
C(19)-C(20)	1.35(2)	C(17)-C(16)-C(21)	118.3(14)
C(20)-C(21)	1.39(3)	C(17)-C(16)-P(1)	118.5(10)
C(22)-C(27)	1.39(2)	C(21)-C(16)-P(1)	123.1(12)
C(22)-C(23)	1.40(2)	C(16)-C(17)-C(18)	122.1(14)
C(23)-C(24)	1.43(2)	C(17)-C(18)-C(19)	118(2)
C(24)-C(25)	1.35(2)	C(20)-C(19)-C(18)	121(2)
C(25)-C(26)	1.37(2)	C(19)-C(20)-C(21)	121(2)
C(26)-C(27)	1.40(2)	C(16)-C(21)-C(20)	121(2)
C(28)-C(29)	1.39(2)	C(27)-C(22)-C(23)	116.1(12)
C(28)-C(33)	1.43(2)	C(27)-C(22)-Pt(1)	122.8(10)
C(29)-C(30)	1.37(2)	C(23)-C(22)-Pt(1)	120.9(10)
C(30)-C(31)	1.39(2)	C(22)-C(23)-C(24)	120.2(13)
C(31)-C(32)	1.37(2)	C(25)-C(24)-C(23)	122(2)
C(32)-C(33)	1.40(2)	C(24)-C(25)-C(26)	119.2(14)
C(34)-C(36)	1.51(2)	C(25)-C(26)-C(27)	119.9(14)
C(34)-C(35)	1.56(3)	C(22)-C(27)-C(26)	123.0(13)
		C(29)-C(28)-C(33)	116.9(12)
C(22)-Pt(1)-C(28)	89.1(5)	C(29)-C(28)-Pt(1)	124.9(10)
C(22)-Pt(1)-N(1)	176.7(5)	C(33)-C(28)-Pt(1)	118.1(10)
C(28)-Pt(1)-N(1)	88.6(4)	C(30)-C(29)-C(28)	122(2)
C(22)-Pt(1)-P(1)	96.8(4)	C(29)-C(30)-C(31)	122(2)
C(28)-Pt(1)-P(1)	171.8(4)	C(32)-C(31)-C(30)	117.5(14)
N(1)-Pt(1)-P(1)	85.7(3)	C(31)-C(32)-C(33)	122.3(14)
C(4)-P(1)-C(16)	103.3(6)	C(32)-C(33)-C(28)	119.3(14)
C(4)-P(1)-C(10)	103.3(5)	C(1)-C(34)-C(36)	113.7(14)
C(16)-P(1)-C(10)	103.8(6)	C(1)-C(34)-C(35)	111.4(14)
C(4)-P(1)-Pt(1)	106.3(4)	C(36)-C(34)-C(35)	110(2)
C(16)-P(1)-Pt(1)	121.4(4)		

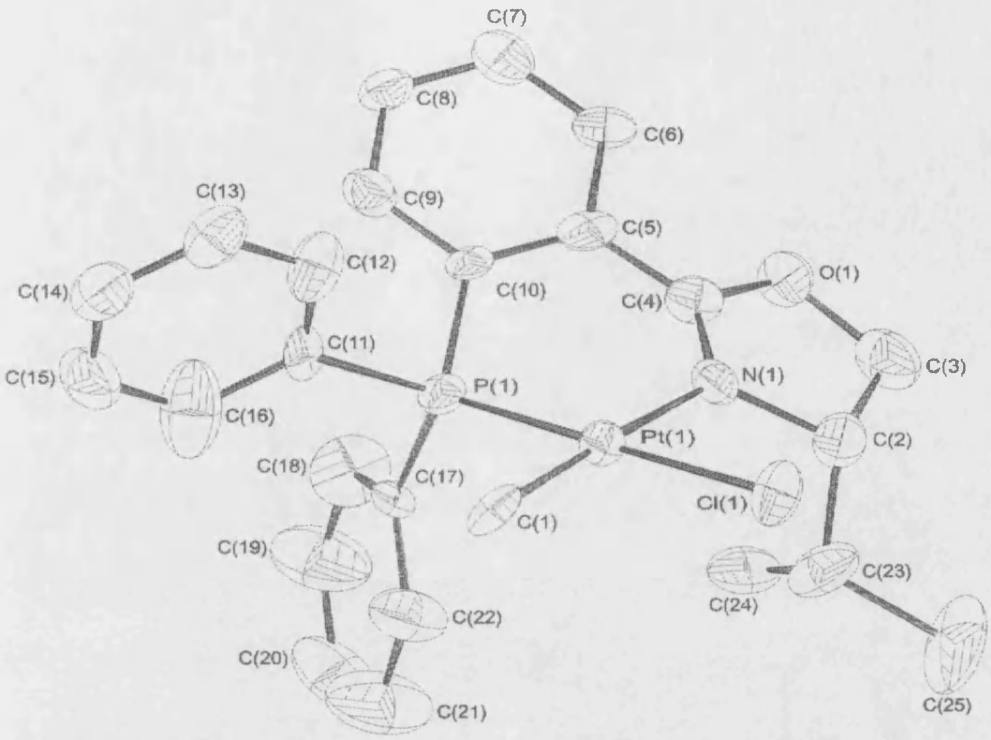
Table 6.4. Anisotropic displacement parameters ($Å^2$ x 10^3) for (75).
The anisotropic displacement factor exponent takes the form:
$-2\ pi^2\ [\ h^2\ a^*\ 2\ U11 + ... + 2\ h\ k\ a^*\ b^*\ U12\ ]$

Atom	U11	U22	U33	U23	U13	U12
Pt(1)	38(1)	38(1)	37(1)	-1(1)	0(1)	2(1)
P(1)	40(2)	40(2)	38(2)	-1(2)	3(1)	3(2)
N(1)	35(6)	56(8)	43(6)	-13(6)	5(5)	5(5)
O(1)	45(5)	64(7)	64(6)	-5(5)	-11(5)	14(5)
C(1)	50(8)	54(9)	49(7)	-4(7)	5(6)	29(7)
C(2)	61(10)	67(11)	91(12)	-22(10)	-21(9)	25(9)
C(3)	29(6)	40(8)	54(8)	2(7)	2(6)	-8(6)
C(4)	44(7)	44(8)	41(7)	-6(6)	13(6)	-21(6)
C(5)	54(9)	33(9)	41(7)	-2(5)	0(7)	-6(5)
C(6)	41(8)	64(9)	69(10)	-6(8)	-7(7)	1(7)
C(7)	74(11)	64(11)	62(10)	-4(8)	-26(8)	-23(9)
C(8)	69(11)	50(9)	84(11)	-16(9)	-12(9)	7(8)
C(9)	50(8)	42(8)	60(8)	-7(7)	-14(7)	1(7)
C(10)	39(5)	17(12)	47(6)	4(5)	2(4)	1(5)
C(11)	65(7)	70(10)	45(6)	-29(16)	6(5)	-3(19)
C(12)	76(11)	71(12)	59(9)	11(9)	27(8)	-5(10)
C(13)	47(8)	58(10)	95(13)	31(10)	2(8)	-17(8)
C(14)	49(11)	69(15)	87(15)	24(12)	-19(10)	-10(10)
C(15)	54(8)	41(8)	46(7)	-6(6)	-13(6)	-7(7)
C(16)	42(7)	47(8)	38(6)	0(6)	-4(5)	2(6)
C(17)	48(8)	51(9)	75(10)	14(8)	10(7)	6(7)
C(18)	78(11)	54(10)	81(11)	9(9)	23(9)	11(9)
C(19)	69(10)	57(10)	72(10)	-5(9)	0(8)	36(9)
C(20)	60(10)	66(12)	124(16)	11(12)	34(11)	15(9)
C(21)	59(11)	38(11)	107(16)	10(10)	29(10)	11(9)
C(22)	40(7)	29(7)	50(7)	-6(6)	-3(6)	2(6)
C(23)	65(10)	36(8)	57(8)	0(7)	14(7)	-4(7)
C(24)	52(9)	41(8)	80(11)	0(8)	-16(8)	6(7)
C(25)	61(9)	46(9)	58(9)	4(7)	-16(7)	18(8)
C(26)	67(10)	40(8)	49(8)	3(6)	-9(7)	17(7)
C(27)	40(7)	42(8)	53(8)	-10(7)	12(6)	-3(6)
C(28)	43(7)	55(8)	35(6)	4(6)	11(5)	9(6)
C(29)	55(8)	45(8)	39(7)	-4(6)	-7(6)	7(7)
C(30)	95(14)	72(12)	55(9)	-16(9)	8(9)	15(10)
C(31)	69(10)	58(10)	70(10)	-7(8)	23(8)	14(8)
C(32)	47(8)	78(11)	63(9)	-1(9)	27(7)	19(8)
C(33)	51(8)	64(10)	60(8)	-3(7)	12(6)	2(7)
C(34)	44(8)	56(9)	74(10)	-3(8)	-12(7)	0(7)
C(35)	92(14)	67(13)	125(18)	-21(12)	-28(13)	10(11)
C(36)	107(16)	78(14)	107(15)	21(12)	31(13)	-3(12)

Table 6.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for (75).

Atom	x	y	z	U(eq)
H(1)	-303(14)	1610(9)	268(14)	61
H(2A)	-2043(18)	1764(12)	-1181(18)	88
H(2B)	-988(18)	2302(12)	-2043(18)	88
H(6)	-1991(16)	-90(10)	-3783(16)	70
H(7)	-1925(19)	-1298(11)	-5001(16)	80
H(8)	-21(18)	-2170(10)	-4885(18)	81
H(9)	1853(15)	-1855(9)	-3458(14)	61
H(11)	3306(13)	-388(25)	-4528(11)	72
H(12)	4584(18)	653(11)	-5740(16)	82
H(13)	5840(17)	1638(10)	-4702(20)	80
H(14)	5824(21)	1714(15)	-2396(22)	82
H(15)	4399(15)	855(8)	-1165(13)	57
H(17)	2467(16)	-2090(10)	-450(16)	70
H(18)	3635(19)	-3364(11)	-526(18)	86
H(19)	5811(18)	-3438(11)	-1638(17)	79
H(20)	6623(19)	-2327(12)	-2803(22)	100
H(21)	5315(22)	-1109(13)	-2894(25)	82
H(23)	4950(16)	-252(9)	719(15)	63
H(24)	6428(17)	-863(10)	2338(17)	69
H(25)	5516(16)	-1722(10)	3918(15)	66
H(26)	3078(16)	-1884(9)	4069(14)	63
H(27)	1587(14)	-1170(9)	2643(13)	54
H(29)	2323(15)	891(9)	2975(12)	56
H(30)	1031(20)	1327(12)	4753(16)	89
H(31)	-1444(18)	1306(10)	4704(17)	78
H(32)	-2558(16)	617(11)	2978(15)	75
H(33)	-1283(15)	105(10)	1181(14)	70
H(34)	2132(16)	1890(10)	-299(16)	70
H(35A)	1685(126)	3413(28)	-383(119)	142
H(35B)	1221(178)	2933(29)	900(31)	142
H(35C)	85(56)	3166(55)	-186(145)	142
H(36A)	2705(87)	2575(99)	-2178(22)	146
H(36B)	1105(102)	2669(90)	-2607(58)	146
H(36C)	1837(182)	1795(18)	-2645(53)	146

X-Ray crystal structure determination of [(S)-P^N]Pt(Me)Cl, (76)



A crystal of approximate dimensions 0.25 x 0.25 x 0.25 mm was used for data collection.

Crystal data: $C_{28.10}H_{27}ClNOPPt$, M = 656.22, Monoclinic , a = 9.697(3), b = 9.740(2), c = 14.739(4) Å , a = 90, b = 101.75(3), g = 90°, U = 1362.9(6) Å^3, space group $P21$, Z = 2, D_c = 1.599 gcm^{-3}, m(Mo-K_a) = 5.324 mm^{-1}, F(000) = 641. Crystallographic measurements were made at 293(2)° K on a CAD4 automatic four-circle diffractometer in the range 2.14<q<23.92°. Data (2266 reflections) were corrected for Lorentz and polarization and also for absorption.[150] (Max. and Min absorption corrections; 1.000, 0.327 respectively).

In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant.

Despite reasonable R factors, this is not a high quality crystal structure. However, no problems were evident prior to, or during the data collection procedure. The refinement was partially hampered by a fragment of disordered solvent in the asymmetric unit, which could not be successfully modelled. Eventually, peaks in this area of the electron density map were treated as partial carbon atoms which were isotropically refined.

Phenyl rings were refined as rigid hexagons, primarily because of shift/esd values pertaining to the ring containing carbons C17-22. In particular, the positions of carbons C18 and C19 did not converge as well as expected in the absence of any restraints. This was surprising as crystal quality was good, and the data collection procedure was trouble free. Smearing of the electron density in the proximity of C18 and C19 was evident in early Difference Fourier maps, prior to any correction for absorption. In fact, the program used for refinement of this structure suggested that these carbon positions should be split between 2 sites which were not structurally meaningful. Hence, this strategy was abandoned.

However, it is reasonable to suggest that there is probably some minor disorder within this phenyl ring, given the larger than average thermal parameters of the atoms therein.

The solution of the structure (SHELX86) [151] and refinement (SHELX93) [152] converged to a conventional [i.e. based on 1773 F^2 data with $Fo>4s(Fo)$] $R1$ = 0.0461 and $wR2$ = 0.1283. Goodness of fit = 1.070. The max. and min. residual densities were 1.012 and -0.757 eÅ^{-3} respectively. The asymmetric unit (shown in Fig. 2.18), along with the labelling scheme used was produced using ORTEX.[60] Final fractional atomic co-ordinates and isotropic thermal parameters, bond distances and angles are given in the supplementary data.

Table 6.6. Crystal data and structure refinement for [(S-P^N)Pt(Me)Cl, (76).

Empirical formula	$C_{28.10}H_{27}$ Cl N O P Pt	Index ranges	-11<=h<=10; 0<=k<=11; 0<=l<=16
Formula weight	656.22	Reflections collected	2266
Temperature	293(2)°K	Independent reflections	2266 [R(int) = 0.0000]
Wavelength	0.70930 Å	Absorption correction	DIFABS
Crystal system	Monoclinic	Max. and min. transmission	1.000 and 0.327
Space group	$P2_1$	Refinement method	Full-matrix least-squares on F^2
Unit cell dimensions	a = 9.697(3)Å	Data / restraints / parameters	2262 / 1 / 236
	b = 9.740(2)Å	Goodness-of-fit on F^2	1.070
	b = 101.75(3)°		
	c = 14.739(4)Å	Final R indices [I>2s(I)]	R1 = 0.0461 wR2 = 0.1283
Volume	1362.9(6) Å^3	R indices (all data)	R1 = 0.0690 wR2 = 0.1473
Z	2	Absolute structure parameter	-0.01(3)
Density (calculated)	1.599 Mg/m^3	Largest diff. peak and hole	1.012 and -0.757 eÅ^{-3}
Absorption coefficient	5.324 mm^{-1}	Weighting scheme	calc $w=1/[\sigma^2(Fo^2)+(0.0880P)^2+0.9764P]$ where $P=(Fo^2+2Fc^2)/3$
F(000)	641		
Crystal size	0.25 x 0.25 x 0.25 mm		
Theta range for data collection	2.14 to 23.92 °.		

Table 6.7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for (76). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Pt(1)	3539(1)	7818(2)	2977(1)	46(1)
P(1)	5750(4)	7859(19)	2872(3)	46(1)
Cl(1)	1165(5)	7717(21)	3112(5)	74(3)
N(1)	3884(19)	5789(18)	3518(11)	53(4)
O(1)	4857(17)	4001(16)	4271(11)	67(4)
C(1)	3107(18)	9799(21)	2398(16)	54(5)
C(2)	2725(23)	4671(26)	3321(17)	69(7)
C(3)	3392(30)	3551(28)	3927(18)	88(8)
C(4)	5008(22)	5263(24)	4000(15)	54(5)
C(5)	6351(10)	5870(14)	4269(9)	54(6)
C(6)	7238(14)	5218(13)	5002(9)	56(6)
C(7)	8627(13)	5647(15)	5279(8)	79(8)
C(8)	9131(10)	6727(16)	4822(10)	60(6)
C(9)	8244(13)	7379(13)	4089(9)	59(6)
C(10)	6855(12)	6951(13)	3812(7)	40(5)
C(11)	6584(13)	9571(13)	2966(12)	58(6)
C(12)	6487(16)	10357(17)	3738(10)	77(8)
C(13)	7038(17)	11678(16)	3828(11)	78(8)
C(14)	7688(18)	12214(13)	3148(14)	82(8)
C(15)	7785(21)	11428(18)	2376(13)	103(11)
C(16)	7233(19)	10106(18)	2285(11)	126(15)
C(17)	6147(13)	7094(13)	1849(9)	58(6)
C(18)	7355(12)	6331(17)	1838(11)	95(11)
C(19)	7538(16)	5707(17)	1022(14)	143(16)
C(20)	6513(22)	5848(20)	218(11)	131(15)
C(21)	5305(19)	6611(20)	229(8)	158(20)
C(22)	5122(14)	7234(14)	1045(10)	94(10)
C(23)	2240(17)	4416(23)	2279(13)	84(8)
C(24)	3615(19)	3765(16)	1959(12)	138(16)
C(25)	660(23)	3632(29)	2017(22)	233(34)
C(26)	1197(22)	7898(33)	321(13)	138(11)
C(27)	-580(21)	7956(29)	905(16)	230(31)
C(28)	-421(21)	9709(29)	308(15)	108(10)
C(29)	359(21)	7949(30)	673(14)	106(19)

Table 6.8. Bond lengths [Å] and angles [°] for (76).

Pt(1)-C(1)	2.12(2)	C(1)-Pt(1)-N(1)	177.3(7)
Pt(1)-N(1)	2.13(2)	C(1)-Pt(1)-P(1)	94.1(7)
Pt(1)-P(1)	2.181(4)	N(1)-Pt(1)-P(1)	87.8(7)
Pt(1)-Cl(1)	2.352(5)	C(1)-Pt(1)-Cl(1)	87.5(7)
P(1)-C(17)	1.792(14)	N(1)-Pt(1)-Cl(1)	90.7(7)
P(1)-C(10)	1.80(2)	P(1)-Pt(1)-Cl(1)	178.4(8)
P(1)-C(11)	1.85(2)	C(17)-P(1)-C(10)	104.3(10)
N(1)-C(4)	1.28(3)	C(17)-P(1)-C(11)	105.8(8)
N(1)-C(2)	1.55(3)	C(10)-P(1)-C(11)	101.7(7)
O(1)-C(4)	1.31(3)	C(17)-P(1)-Pt(1)	115.8(5)
O(1)-C(3)	1.47(3)	C(10)-P(1)-Pt(1)	112.1(6)
C(2)-C(3)	1.47(3)	C(11)-P(1)-Pt(1)	115.7(9)
C(2)-C(23)	1.53(3)	C(4)-N(1)-C(2)	109(2)
C(4)-C(5)	1.41(2)	C(4)-N(1)-Pt(1)	129(2)
C(23)-C(24)	1.63	C(2)-N(1)-Pt(1)	121.9(14)
C(23)-C(25)	1.68(2)	C(4)-O(1)-C(3)	110(2)
C(26)-C(29)	1.05	C(3)-C(2)-C(23)	120(2)
C(27)-C(29)	1.04	C(3)-C(2)-N(1)	101(2)
C(27)-C(28)	1.942(3)	C(23)-C(2)-N(1)	111(2)
C(28)-C(29)	1.907(3)	C(2)-C(3)-O(1)	105(2)
		N(1)-C(4)-O(1)	114(2)
		N(1)-C(4)-C(5)	128(2)
		O(1)-C(4)-C(5)	118(2)
		C(6)-C(5)-C(10)	120.0
		C(6)-C(5)-C(4)	114.6(13)
		C(10)-C(5)-C(4)	125.2(12)
		C(9)-C(10)-P(1)	117.9(8)
		C(5)-C(10)-P(1)	122.1(8)
		C(12)-C(11)-C(16)	120.0
		C(12)-C(11)-P(1)	117.2(9)
		C(16)-C(11)-P(1)	122.7(9)
		C(18)-C(17)-P(1)	123.9(9)
		C(22)-C(17)-P(1)	116.0(9)
		C(2)-C(23)-C(24)	104.5(13)
		C(2)-C(23)-C(25)	113(2)
		C(24)-C(23)-C(25)	121(2)
		C(29)-C(27)-C(28)	72.5(3)
		C(29)-C(28)-C(27)	31.2
		C(27)-C(29)-C(26)	169.70(11)
		C(27)-C(29)-C(28)	76.3(3)
		C(26)-C(29)-C(28)	101.9(4)

Symmetry transformations used to generate equivalent atoms:

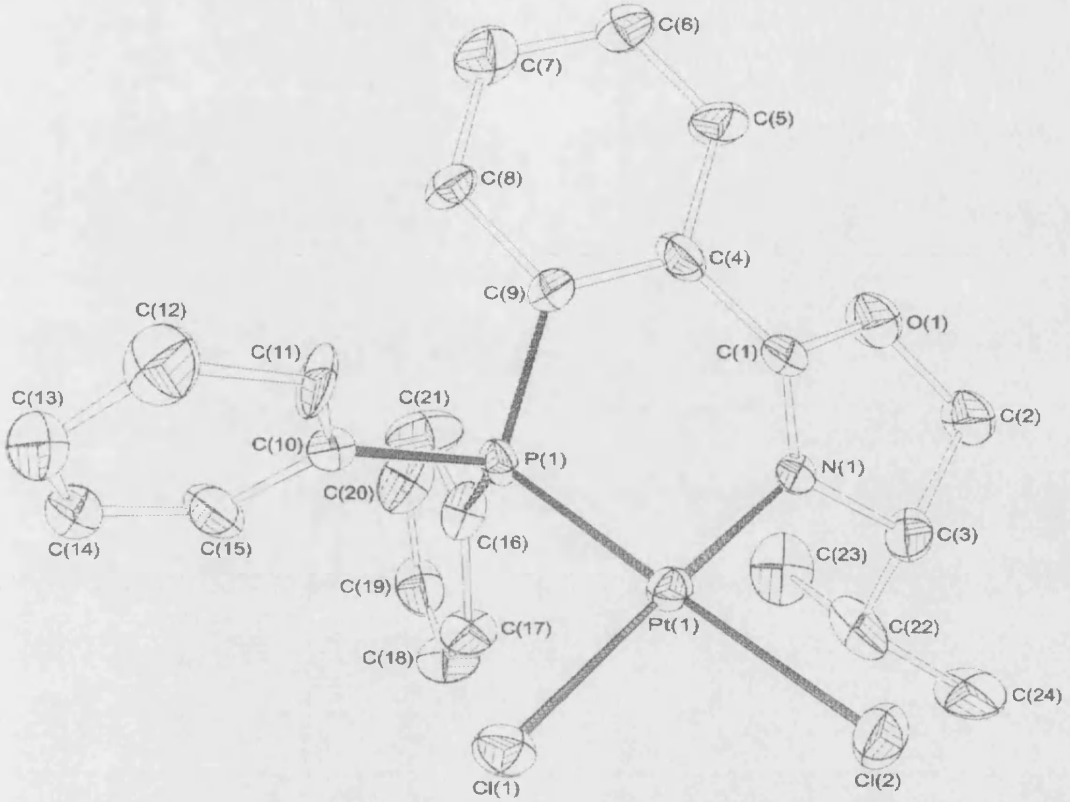
Table 6.9. Anisotropic displacement parameters ($Å^2$ x 10^3) for (76).
The anisotropic displacement factor exponent takes the form:
$-2\ pi^2\ [\ h^2\ a^*\ 2\ U11 + ... + 2\ h\ k\ a^*\ b^*\ U12\ ]$

Atom	U11	U22	U33	U23	U13	U12
Pt(1)	47(1)	45(1)	46(1)	-1(1)	10(1)	-3(1)
P(1)	44(2)	54(2)	39(2)	-16(8)	9(2)	-8(8)
Cl(1)	47(2)	77(7)	103(4)	-7(6)	26(2)	-7(5)
N(1)	77(12)	48(10)	37(10)	-2(9)	17(9)	-16(10)
O(1)	77(10)	44(9)	75(10)	21(8)	1(8)	-2(8)
C(1)	29(9)	45(12)	79(16)	-12(12)	-10(10)	-2(9)
C(2)	54(12)	68(15)	79(17)	25(14)	0(12)	-1(12)
C(3)	137(25)	55(14)	71(17)	12(14)	18(16)	-11(17)
C(4)	51(12)	58(14)	52(13)	3(11)	7(10)	17(11)
C(5)	50(12)	78(16)	35(12)	-31(12)	11(10)	3(12)
C(6)	57(12)	60(14)	46(13)	6(11)	-6(10)	21(11)
C(7)	89(18)	101(21)	53(15)	-10(15)	28(13)	-3(16)
C(8)	40(11)	86(17)	49(13)	-5(13)	-3(10)	-4(11)
C(9)	70(14)	56(14)	50(13)	13(9)	10(11)	2(10)
C(10)	40(10)	54(13)	27(10)	-20(9)	5(8)	-8(9)
C(11)	9(7)	83(16)	79(16)	39(14)	4(8)	7(9)
C(12)	59(14)	61(17)	117(26)	-20(17)	32(16)	-5(12)
C(13)	64(15)	57(15)	106(23)	-4(16)	-1(15)	1(13)
C(14)	72(16)	77(16)	90(21)	2(16)	-1(15)	-6(14)
C(15)	157(31)	80(21)	71(20)	8(17)	23(19)	-44(21)
C(16)	96(24)	76(24)	218(47)	29(27)	64(28)	8(20)
C(17)	68(14)	81(15)	25(11)	0(10)	10(10)	-28(12)
C(18)	75(18)	105(25)	114(25)	-35(20)	38(17)	42(18)
C(19)	222(47)	122(32)	80(24)	-18(24)	22(27)	25(33)
C(20)	208(42)	132(31)	76(23)	-10(23)	81(27)	23(32)
C(21)	149(35)	250(58)	77(26)	-30(32)	30(24)	62(39)
C(22)	90(18)	133(28)	58(16)	0(15)	14(14)	32(17)
C(23)	87(18)	51(15)	95(20)	-9(15)	-23(16)	-11(14)
C(24)	181(35)	179(38)	43(15)	-26(21)	1(18)	-88(32)
C(25)	279(52)	279(69)	178(40)	-158(43)	131(38)	-230(53)

Table 6.10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for (76).

Atom	x	y	z	U(eq)
H(1A)	3103(153)	9766(38)	1746(26)	81
H(1B)	3819(89)	10428(38)	2695(73)	81
H(1C)	2202(72)	10100(66)	2490(91)	81
H(2)	1913(23)	4999(26)	3560(17)	83
H(3A)	3368(30)	2699(28)	3583(18)	106
H(3B)	2914(30)	3412(28)	4438(18)	106
H(6)	6901(19)	4496(16)	5308(12)	68
H(7)	9220(17)	5210(21)	5770(11)	95
H(8)	10060(11)	7013(22)	5007(13)	72
H(9)	8581(18)	8101(17)	3783(13)	71
H(12)	6052(24)	9998(23)	4193(13)	92
H(13)	6973(26)	12204(22)	4345(14)	94
H(14)	8057(25)	13098(15)	3209(19)	99
H(15)	8220(30)	11786(25)	1921(16)	123
H(16)	7299(28)	9580(24)	1769(13)	151
H(18)	8040(12)	6237(23)	2376(13)	115
H(19)	8346(19)	5197(20)	1015(20)	171
H(20)	6635(28)	5431(25)	-328(13)	158
H(21)	4620(22)	6705(26)	-309(8)	189
H(22)	4314(15)	7745(15)	1052(14)	113
H(23)	2102(14)	5326(23)	1991(15)	100
H(24A)	3379(98)	2881(144)	1682(201)	207
H(24B)	4367(111)	3667(305)	2490(37)	207
H(24C)	3908(204)	4363(162)	1516(166)	207
H(25A)	652(32)	2862(44)	2422(40)	350
H(25B)	491(24)	3320(42)	1386(30)	350
H(25C)	-64(25)	4268(35)	2093(17)	350

Crystal structure determination for [(S)-P^N]$PtCl_2$, (66)



A crystal of approximate dimensions 0.25 x 0.25 x 0.15 mm was used for data collection. [*Crystal data:* $C_{24}H_{24}Cl_2NOPPt$, M = 639.40, Monoclinic , a = 9.997(3), b = 12.855(2), c = 10.545(2) Å , β = 112.10(2)°, U = 1255.6(5) Å^3, space group $P2_1$, Z = 2, D_c = 1.691 gcm^{-3}, μ(Mo-K_α) = 5.879 mm^{-1}, F(000) = 620.] Crystallographic measurements were made at 293(2)° K on a CAD4 automatic four-circle diffractometer in the range 2.08<θ<23.93°. Data (2063 reflections) were corrected for Lorentz and polarization and also for absorption.[150] (Maximum and Minimum absorption corrections; 1.000, 0.246 respectively). In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant. The solution of the structure (SHELX86)[151] and refinement (SHELX93)[152] converged to a conventional [i.e. based on 1846 with $Fo>4\sigma(Fo)$] $R1$ = 0.0495 and $wR2$ = 0.1394. Goodness of fit = 1.019. The max. and min. residual densities were 2.821 and -2.385eÅ^{-3} respectively. The asymmetric unit (shown in Fig. 3.23), along with the labelling scheme used was produced using ORTEX.[60]

Table 6.11. Crystal data and structure refinement for (66).

Empirical formula	$C_{24}H_{24}Cl_2NOPPt$	Theta range for data collection	2.08 to 23.93°
Formula weight	639.40	Index ranges	-11<=h<=10; 0<=k<=14; 0<=l<=12
Temperature	293(2)°K	Reflections collected	2063
Wavelength	0.71069 Å	Independent reflections	2063 [R(int) = 0.0000]
Crystal system	Monoclinic	Absorption correction	DIFABS
Space group	$P2_1$	Max. and min. transmission	1.000 and 0.246
Unit cell dimensions	a = 9.997(3)Å	Refinement method	Full-matrix least-squares on F^2
	b = 12.855(2)Å β= 112.10(2)°	Data / restraints / parameters	2062 / 1 / 274
	c = 10.545(2)Å	Goodness-of-fit on F^2	1.019
Volume	1255.6(5) Å^3	Final R indices [I>2σ(I)]	R1 = 0.0495 wR2 = 0.1394
Z	2	R indices (all data)	R1 = 0.0601 wR2 = 0.1602
Density (calculated)	1.691 Mg/m^3	Abs. Structure parameter	-0.01(3)
Absorption coefficient	5.879 mm^{-1}	Largest diff. peak and hole	2.821 and -2.385 eÅ^{-3}
F(000)	620	Weighting scheme	calc $w=1/[\sigma^2(Fo^2)+(0.1220P)^2+5.7835P]$ where $P=(Fo^2+2Fc^2)/3$
Crystal size	0.25 x 0.25 x 0.15 mm	Extinction coefficient	0.0006(8)

Table 6.12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for (66). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Pt(1)	2866(1)	7837(1)	9790(1)	32(1)
Cl(1)	2038(6)	8990(5)	10974(5)	46(1)
Cl(2)	4671(7)	7301(5)	11877(6)	53(1)
P(1)	1280(5)	8404(4)	7844(5)	31(1)
O(1)	3947(23)	5863(15)	7144(21)	63(5)
N(1)	3517(16)	6750(14)	8784(18)	35(4)
C(1)	3499(24)	6757(19)	7558(25)	44(5)
C(2)	4506(33)	5215(23)	8318(32)	64(8)
C(3)	3966(25)	5673(19)	9378(28)	49(6)
C(4)	2962(26)	7556(19)	6495(24)	49(8)
C(5)	3492(33)	7484(22)	5406(27)	56(7)
C(6)	3068(31)	8203(30)	4415(31)	80(13)
C(7)	2045(30)	9013(24)	4394(25)	58(7)
C(8)	1541(25)	9051(18)	5439(22)	42(5)
C(9)	2007(24)	8321(19)	6510(22)	40(5)
C(10)	790(25)	9779(17)	7826(23)	39(5)
C(11)	1785(28)	10515(17)	8051(30)	49(7)
C(12)	1510(38)	11568(24)	8102(32)	66(8)
C(13)	93(45)	11804(24)	7966(37)	80(10)
C(14)	-916(35)	11095(23)	7778(34)	65(8)
C(15)	-627(29)	10045(25)	7676(27)	57(7)
C(16)	-343(23)	7612(14)	7215(22)	43(6)
C(17)	-836(25)	7217(23)	8205(29)	54(7)
C(18)	-2068(35)	6618(23)	7782(33)	65(7)
C(19)	-2846(35)	6437(25)	6504(45)	78(10)
C(20)	-2455(37)	6871(32)	5494(39)	87(12)
C(21)	-1174(35)	7511(30)	5866(31)	84(12)
C(22)	2812(30)	5130(18)	9631(32)	61(9)
C(23)	1525(40)	4810(29)	8270(46)	85(12)
C(24)	3428(46)	4138(27)	10488(44)	90(12)

Table 6.13. Bond lengths [Å] and angles [°] for (66).

Pt(1)-N(1)	2.01(2)	C(9)-P(1)-Pt(1)	110.3(7)
Pt(1)-P(1)	2.192(5)	C(16)-P(1)-Pt(1)	112.8(7)
Pt(1)-Cl(1)	2.284(6)	C(10)-P(1)-Pt(1)	115.2(8)
Pt(1)-Cl(2)	2.363(6)	C(1)-O(1)-C(2)	107(2)
P(1)-C(9)	1.81(2)	C(1)-N(1)-C(3)	108(2)
P(1)-C(16)	1.82(2)	C(1)-N(1)-Pt(1)	130(2)
P(1)-C(10)	1.83(2)	C(3)-N(1)-Pt(1)	122(2)
O(1)-C(1)	1.36(3)	N(1)-C(1)-O(1)	116(2)
O(1)-C(2)	1.42(4)	N(1)-C(1)-C(4)	130(2)
N(1)-C(1)	1.29(3)	O(1)-C(1)-C(4)	115(2)
N(1)-C(3)	1.52(3)	O(1)-C(2)-C(3)	106(2)
C(1)-C(4)	1.47(3)	C(22)-C(3)-N(1)	112(2)
C(2)-C(3)	1.53(4)	C(22)-C(3)-C(2)	118(2)
C(3)-C(22)	1.46(3)	N(1)-C(3)-C(2)	100(2)
C(4)-C(9)	1.37(3)	C(9)-C(4)-C(5)	121(2)
C(4)-C(5)	1.44(3)	C(9)-C(4)-C(1)	123(2)
C(5)-C(6)	1.34(4)	C(5)-C(4)-C(1)	115(2)
C(6)-C(7)	1.45(4)	C(6)-C(5)-C(4)	118(3)
C(7)-C(8)	1.37(4)	C(5)-C(6)-C(7)	121(2)
C(8)-C(9)	1.41(3)	C(8)-C(7)-C(6)	119(2)
C(10)-C(11)	1.33(3)	C(7)-C(8)-C(9)	121(2)
C(10)-C(15)	1.41(3)	C(4)-C(9)-C(8)	119(2)
C(11)-C(12)	1.39(4)	C(4)-C(9)-P(1)	122(2)
C(12)-C(13)	1.40(5)	C(8)-C(9)-P(1)	118(2)
C(13)-C(14)	1.32(5)	C(11)-C(10)-C(15)	120(2)
C(14)-C(15)	1.39(4)	C(11)-C(10)-P(1)	120(2)
C(16)-C(21)	1.36(4)	C(15)-C(10)-P(1)	119(2)
C(16)-C(17)	1.41(3)	C(10)-C(11)-C(12)	124(3)
C(17)-C(18)	1.38(4)	C(11)-C(12)-C(13)	115(3)
C(18)-C(19)	1.30(5)	C(14)-C(13)-C(12)	124(3)
C(19)-C(20)	1.38(5)	C(13)-C(14)-C(15)	121(3)
C(20)-C(21)	1.45(4)	C(14)-C(15)-C(10)	117(3)
C(22)-C(24)	1.55(4)	C(21)-C(16)-C(17)	120(2)
C(22)-C(23)	1.58(5)	C(21)-C(16)-P(1)	123(2)
		C(17)-C(16)-P(1)	117(2)
N(1)-Pt(1)-P(1)	90.0(5)	C(18)-C(17)-C(16)	119(3)
N(1)-Pt(1)-Cl(1)	176.1(5)	C(19)-C(18)-C(17)	123(3)
P(1)-Pt(1)-Cl(1)	90.8(2)	C(18)-C(19)-C(20)	120(3)
N(1)-Pt(1)-Cl(2)	90.2(5)	C(19)-C(20)-C(21)	120(3)
P(1)-Pt(1)-Cl(2)	176.6(2)	C(16)-C(21)-C(20)	118(3)
Cl(1)-Pt(1)-Cl(2)	89.2(2)	C(3)-C(22)-C(24)	109(2)
C(9)-P(1)-C(16)	104.3(11)	C(3)-C(22)-C(23)	113(3)
C(9)-P(1)-C(10)	103.4(10)	C(24)-C(22)-C(23)	109(3)
C(16)-P(1)-C(10)	109.7(10)		

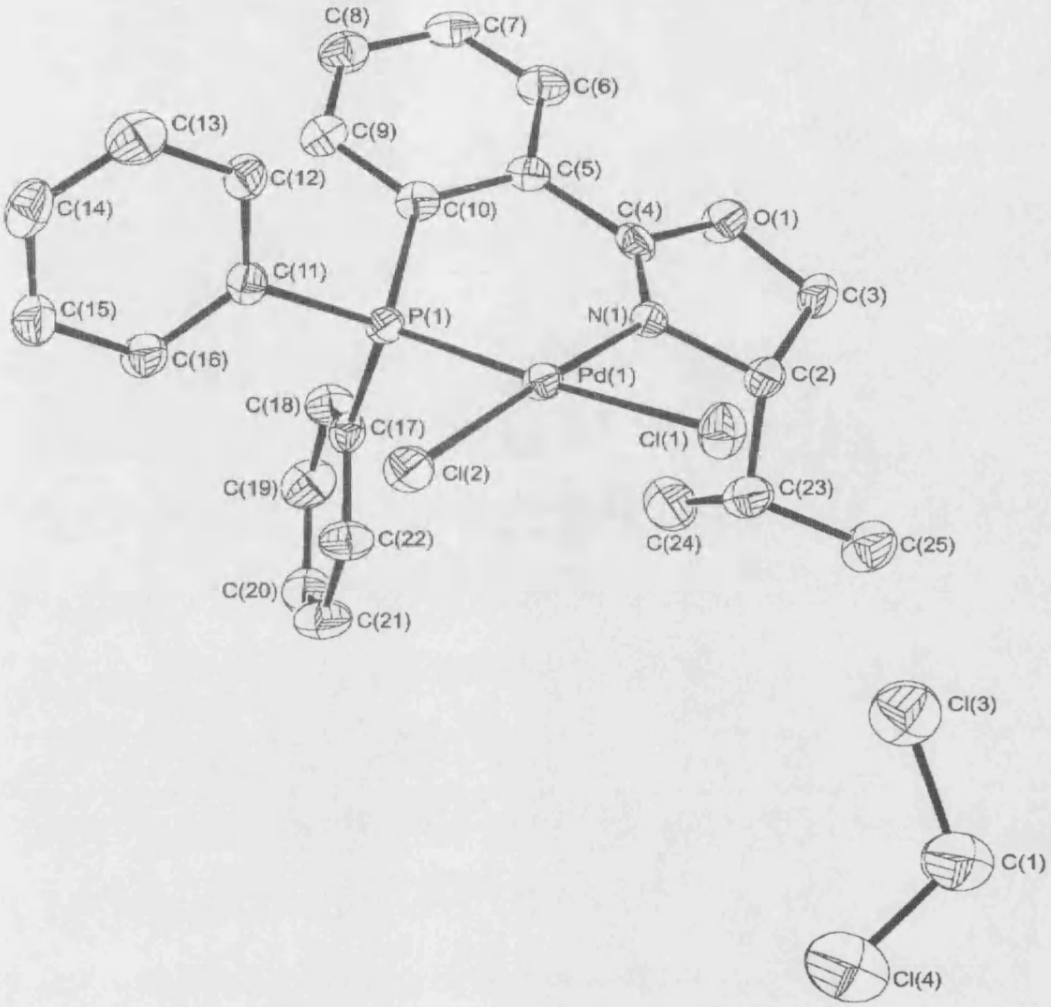
Table 6.14. Anisotropic displacement parameters ($Å^2$ x 10^3) for (66).
The anisotropic displacement factor exponent takes the form:
$-2\ pi^2$ [h2 a* 2 U11 + ... + 2 h k a* b* U12]

Atom	U11	U22	U33	U23	U13	U12
Pt(1)	28(1)	36(1)	29(1)	2(1)	9(1)	0(1)
Cl(1)	51(3)	54(3)	35(3)	-7(2)	18(2)	-1(3)
Cl(2)	49(3)	59(3)	40(3)	1(3)	4(2)	12(3)
P(1)	31(2)	31(2)	30(2)	-6(2)	10(2)	6(2)
O(1)	79(13)	53(10)	73(12)	2(10)	47(11)	23(10)
N(1)	16(7)	45(9)	47(10)	18(8)	16(7)	0(7)
C(1)	36(11)	52(13)	54(14)	8(12)	29(11)	3(10)
C(2)	71(18)	53(15)	83(20)	0(15)	45(16)	21(14)
C(3)	36(12)	50(13)	60(15)	21(12)	17(11)	1(10)
C(4)	41(13)	71(22)	44(12)	-3(10)	25(10)	10(11)
C(5)	78(18)	66(16)	41(14)	9(12)	41(14)	21(13)
C(6)	69(16)	132(38)	53(15)	46(20)	38(13)	32(18)
C(7)	67(17)	67(16)	33(12)	8(12)	13(12)	1(14)
C(8)	54(13)	39(11)	35(11)	12(10)	18(10)	5(11)
C(9)	41(11)	44(11)	35(11)	10(9)	14(9)	3(10)
C(10)	51(13)	35(11)	40(11)	6(10)	27(10)	10(10)
C(11)	41(13)	18(11)	78(18)	16(12)	13(12)	8(10)
C(12)	87(23)	43(15)	67(19)	-18(14)	30(16)	-10(16)
C(13)	126(29)	45(15)	94(24)	12(16)	71(23)	27(19)
C(14)	76(19)	56(16)	86(21)	23(15)	57(18)	27(15)
C(15)	51(15)	74(17)	55(15)	-6(14)	28(12)	8(13)
C(16)	32(10)	36(17)	39(11)	-13(8)	-10(9)	-9(8)
C(17)	32(12)	74(17)	62(16)	14(14)	24(12)	-15(12)
C(18)	82(20)	55(15)	68(18)	-5(15)	39(17)	-25(15)
C(19)	58(17)	57(17)	129(32)	-1(20)	47(20)	-11(14)
C(20)	61(17)	89(25)	75(21)	2(19)	-18(16)	-17(18)
C(21)	70(18)	122(33)	61(17)	13(17)	25(15)	-42(18)
C(22)	80(20)	16(10)	112(25)	-8(12)	64(20)	7(11)
C(23)	70(22)	48(21)	133(34)	0(22)	34(21)	-26(19)
C(24)	127(29)	66(19)	112(28)	45(21)	87(26)	24(21)

Table 6.15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for (66).

Atom	x	y	z	U(eq)
H(2A)	5553(33)	5211(23)	8669(32)	77
H(2B)	4163(33)	4507(23)	8093(32)	77
H(3)	4790(25)	5743(19)	10249(28)	59
H(5)	4114(33)	6951(22)	5389(27)	67
H(6)	3436(31)	8184(30)	3726(31)	96
H(7)	1738(30)	9496(24)	3686(25)	69
H(8)	885(25)	9564(18)	5438(22)	51
H(11)	2721(28)	10312(17)	8181(30)	58
H(12)	2208(38)	12076(24)	8218(32)	79
H(13)	-148(45)	12498(24)	8011(37)	96
H(14)	-1833(35)	11299(23)	7713(34)	78
H(15)	-1340(29)	9541(25)	7515(27)	69
H(17)	-338(25)	7358(23)	9129(29)	64
H(18)	-2358(35)	6328(23)	8446(33)	78
H(19)	-3662(35)	6018(25)	6270(45)	94
H(20)	-3015(37)	6752(32)	4576(39)	105
H(21)	-928(35)	7844(30)	5201(31)	101
H(22)	2434(30)	5589(18)	10160(32)	74
H(23A)	771(141)	5320(130)	8059(173)	128
H(23B)	1157(220)	4144(114)	8391(113)	128
H(23C)	1866(83)	4773(227)	7533(80)	128
H(24A)	3632(312)	3626(90)	9923(89)	134
H(24B)	2733(140)	3865(139)	10827(268)	134
H(24C)	4301(183)	4309(53)	11244(179)	134

Crystal structure determination for [(S)-P^N]$PdCl_2$, (156)



A crystal of approximate dimensions 0.3 x 0.3 x 0.3 mm was used for data collection.

Crystal data: $C_{25}H_{26}Cl_4NOPPd$, M = 635.64, Monoclinic , a = 10.218(4), b = 12.815(2), c = 10.729(3) Å , β = 111.27(3)°, U = 1309.2(7) Å^3, space group $P2_1$, Z = 2, D_c = 1.612 gcm^{-3}, μ(Mo-K_α) = 1.197 mm^{-1}, F(000) = 640. Crystallographic measurements were made at 293(2) K on a CAD4 automatic four-circle diffractometer in the range 2.03<θ<23.91°. Data (2336 reflections) were corrected for Lorentz, polarization and 8% decay of the crystal in the X-ray beam but not for absorption. The asymmetric unit was seen to consist of one molecule of the palladium complex and one molecule of dichloromethane. In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant. The solution of the structure (SHELX86)[151] and refinement (SHELX93)[152] converged to a conventional [i.e. based on 1932 F^2 data with $Fo>4\sigma(Fo)$] RI = 0.0484 and $wR2$ = 0.1173. Goodness of fit = 1.127. The maximum and minimum residual densities were 1.301 and -0.632 eÅ^{-3} respectively. The asymmetric unit (shown in Fig. 3.24), along with the labelling scheme used was produced using ORTEX.[60]

Table 6.16. Crystal data and structure refinement for (156).

Empirical formula	$C_{25}H_{26}Cl_4NOPPd$	Theta range for data collection	2.03 to 23.91 °.
Formula weight	635.64	Index ranges	-11<=h<=0; -14<=k<=0; -11<=l<=12
Temperature	293(2)°K	Reflections collected	2336
Wavelength	0.71069 Å	Independent reflections	2159 [R(int) = 0.0189]
Crystal system	Monoclinic	Refinement method	Full-matrix least-squares on F^2
Space group	$P2_1$	Data / restraints / parameters	2151 / 1 / 300
Unit cell dimensions	a = 10.218(4)Å b = 12.815(2)Å b = 111.27(3)° c = 10.729(3)Å	Goodness-of-fit on F^2	1.127
		Final R indices [I>2σ(I)]	R1 = 0.0484 wR2 = 0.1173
		R indices (all data)	R1 = 0.0623 wR2 = 0.1385
Volume	1309.2(7) Å^3	Abs. structure parameter	0.00
Z	2	Largest diff. peak and hole	1.301 and -0.632 eÅ^{-3}
Density (calculated)	1.612 Mg/m^3	Weighting scheme	calc $w=1/[s^2(Fo^2)+(0.0834P)^2]$ where $P=(Fo^2+2Fc^2)/3$
Absorption coefficient	1.197 mm^{-1}		
F(000)	640		
Crystal size	0.3 x 0.3 x 0.3 mm		

Table 6.17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for (156). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Pd(1)	2958(1)	6031(1)	5037(1)	32(1)
Cl(1)	4698(3)	5561(3)	7127(3)	52(1)
Cl(2)	1960(3)	7154(2)	6102(3)	46(1)
Cl(3)	4259(4)	3242(4)	9080(4)	91(1)
Cl(4)	2278(5)	2680(5)	10353(5)	104(2)
P(1)	1446(3)	6585(2)	3089(2)	33(1)
N(1)	3667(8)	4963(6)	4029(7)	31(2)
O(1)	4386(8)	4148(6)	2580(7)	48(2)
C(1)	3717(19)	2325(17)	10043(19)	99(6)
C(2)	4200(10)	3941(8)	4691(10)	36(2)
C(3)	4849(12)	3478(9)	3735(11)	49(3)
C(4)	3738(10)	4956(8)	2887(11)	38(2)
C(5)	3139(10)	5718(7)	1765(10)	36(2)
C(6)	3545(12)	5626(10)	669(11)	51(3)
C(7)	2941(12)	6241(10)	-437(12)	51(4)
C(8)	1957(12)	6972(11)	-471(12)	52(3)
C(9)	1557(11)	7097(9)	600(10)	45(3)
C(10)	2137(10)	6466(9)	1766(10)	39(2)
C(11)	983(10)	7972(8)	3032(10)	37(2)
C(12)	1952(12)	8687(8)	3010(12)	45(3)
C(13)	1649(14)	9738(11)	2977(13)	60(3)
C(14)	394(14)	10079(10)	2976(12)	57(3)
C(15)	-611(14)	9347(10)	3007(13)	58(3)
C(16)	-303(12)	8294(9)	3051(11)	46(3)
C(17)	-153(10)	5807(7)	2562(10)	36(3)
C(18)	-746(11)	5417(9)	1276(11)	47(3)
C(19)	-1911(14)	4801(11)	959(14)	64(3)
C(20)	-2498(13)	4531(10)	1903(13)	59(3)
C(21)	-1889(13)	4929(10)	3150(14)	59(3)
C(22)	-723(11)	5528(10)	3461(11)	49(3)
C(23)	3074(13)	3288(10)	4940(12)	54(3)
C(24)	1825(15)	3085(12)	3711(18)	77(4)
C(25)	3744(15)	2290(11)	5662(14)	65(4)

Table 6.18. Bond lengths [Å] and angles [°] for (156).

Pd(1)-N(1)	2.034(8)	C(6)-C(7)	1.37(2)
Pd(1)-P(1)	2.217(3)	C(7)-C(8)	1.36(2)
Pd(1)-Cl(2)	2.294(3)	C(8)-C(9)	1.36(2)
Pd(1)-Cl(1)	2.379(3)	C(9)-C(10)	1.43(2)
Cl(3)-C(1)	1.78(2)	C(11)-C(12)	1.36(2)
Cl(4)-C(1)	1.68(2)	C(11)-C(16)	1.385(14)
P(1)-C(10)	1.806(10)	C(12)-C(13)	1.38(2)
P(1)-C(17)	1.821(9)	C(13)-C(14)	1.36(2)
P(1)-C(11)	1.835(11)	C(14)-C(15)	1.40(2)
N(1)-C(4)	1.254(13)	C(15)-C(16)	1.38(2)
N(1)-C(2)	1.496(13)	C(17)-C(22)	1.34(2)
O(1)-C(4)	1.332(12)	C(17)-C(18)	1.383(14)
O(1)-C(3)	1.439(13)	C(18)-C(19)	1.37(2)
C(2)-C(23)	1.52(2)	C(19)-C(20)	1.39(2)
C(2)-C(3)	1.529(14)	C(20)-C(21)	1.35(2)
C(4)-C(5)	1.498(14)	C(21)-C(22)	1.35(2)
C(5)-C(6)	1.387(14)	C(23)-C(24)	1.49(2)
C(5)-C(10)	1.402(14)	C(23)-C(25)	1.52(2)

N(1)-Pd(1)-P(1)	88.6(2)	C(7)-C(6)-C(5)	120.4(12)
N(1)-Pd(1)-Cl(2)	174.6(2)	C(8)-C(7)-C(6)	120.9(11)
P(1)-Pd(1)-Cl(2)	89.16(10)	C(9)-C(8)-C(7)	120.2(11)
N(1)-Pd(1)-Cl(1)	92.4(2)	C(8)-C(9)-C(10)	121.1(11)
P(1)-Pd(1)-Cl(1)	175.17(12)	C(5)-C(10)-C(9)	117.3(9)
Cl(2)-Pd(1)-Cl(1)	90.26(10)	C(5)-C(10)-P(1)	123.5(8)
C(10)-P(1)-C(17)	105.8(5)	C(9)-C(10)-P(1)	119.0(8)
C(10)-P(1)-C(11)	103.0(5)	C(12)-C(11)-C(16)	120.2(10)
C(17)-P(1)-C(11)	109.2(4)	C(12)-C(11)-P(1)	118.3(7)
C(10)-P(1)-Pd(1)	112.1(3)	C(16)-C(11)-P(1)	121.5(8)
C(17)-P(1)-Pd(1)	110.9(3)	C(11)-C(12)-C(13)	120.1(11)
C(11)-P(1)-Pd(1)	115.1(3)	C(14)-C(13)-C(12)	121.3(12)
C(4)-N(1)-C(2)	108.5(8)	C(13)-C(14)-C(15)	119.1(11)
C(4)-N(1)-Pd(1)	133.1(7)	C(16)-C(15)-C(14)	119.7(12)
C(2)-N(1)-Pd(1)	118.4(6)	C(15)-C(16)-C(11)	119.7(11)
C(4)-O(1)-C(3)	106.8(8)	C(22)-C(17)-C(18)	118.2(9)
Cl(4)-C(1)-Cl(3)	114.5(12)	C(22)-C(17)-P(1)	119.8(8)
N(1)-C(2)-C(23)	113.4(8)	C(18)-C(17)-P(1)	121.8(8)
N(1)-C(2)-C(3)	101.1(7)	C(19)-C(18)-C(17)	118.9(11)
C(23)-C(2)-C(3)	116.3(9)	C(18)-C(19)-C(20)	121.9(12)
O(1)-C(3)-C(2)	105.0(8)	C(21)-C(20)-C(19)	117.3(12)
N(1)-C(4)-O(1)	117.2(9)	C(22)-C(21)-C(20)	120.4(11)
N(1)-C(4)-C(5)	128.9(9)	C(17)-C(22)-C(21)	123.1(11)
O(1)-C(4)-C(5)	113.8(9)	C(24)-C(23)-C(2)	113.6(10)
C(6)-C(5)-C(10)	120.1(10)	C(24)-C(23)-C(25)	112.8(12)
C(6)-C(5)-C(4)	117.7(9)	C(2)-C(23)-C(25)	108.8(9)
C(10)-C(5)-C(4)	122.1(8)		

Table 6.19. Anisotropic displacement parameters ($Å^2$ x 10^3) for (156).
The anisotropic displacement factor exponent takes the form:
$-2\ pi^2\ [\ h^2\ a^*\ 2\ U11 + ... + 2\ h\ k\ a^*\ b^*\ U12\ ]$

Atom	U11	U22	U33	U23	U13	U12
Pd(1)	38(1)	29(1)	32(1)	0(1)	15(1)	1(1)
Cl(1)	55(2)	57(2)	37(1)	-1(1)	10(1)	10(1)
Cl(2)	60(2)	42(2)	44(1)	-3(1)	28(1)	6(1)
Cl(3)	102(3)	93(3)	80(2)	-5(2)	36(2)	2(3)
Cl(4)	85(3)	140(5)	82(3)	-32(3)	25(2)	-28(3)
P(1)	38(1)	30(1)	33(1)	0(1)	16(1)	2(1)
N(1)	34(4)	32(5)	29(4)	0(3)	15(3)	4(3)
O(1)	68(5)	37(4)	46(4)	0(3)	31(4)	9(4)
C(1)	104(13)	102(14)	107(14)	13(12)	59(11)	9(11)
C(2)	39(5)	32(6)	36(5)	-1(5)	12(4)	0(5)
C(3)	57(6)	39(6)	56(7)	12(6)	26(6)	15(5)
C(4)	33(5)	33(6)	57(7)	-4(5)	25(5)	4(4)
C(5)	39(5)	35(6)	39(5)	-5(4)	19(4)	-6(4)
C(6)	59(7)	58(7)	44(6)	-4(6)	30(6)	-2(6)
C(7)	63(6)	58(11)	42(6)	1(6)	31(5)	-12(6)
C(8)	57(7)	57(8)	41(6)	4(6)	16(5)	-5(6)
C(9)	52(6)	41(6)	42(6)	4(5)	17(5)	-3(6)
C(10)	43(6)	37(5)	39(6)	-4(5)	16(5)	-3(5)
C(11)	42(6)	38(6)	32(5)	-1(5)	13(4)	6(5)
C(12)	42(6)	27(6)	66(8)	1(5)	20(5)	-1(5)
C(13)	65(8)	48(8)	63(8)	-6(7)	19(6)	-15(7)
C(14)	77(9)	34(6)	57(7)	1(5)	22(6)	13(6)
C(15)	67(8)	49(8)	66(8)	11(6)	33(7)	22(6)
C(16)	60(7)	33(6)	52(6)	0(5)	29(6)	4(5)
C(17)	36(5)	25(7)	42(5)	0(4)	10(4)	1(4)
C(18)	48(6)	46(7)	47(6)	-4(6)	16(5)	-11(6)
C(19)	72(8)	51(8)	63(8)	-6(7)	16(7)	-16(7)
C(20)	49(6)	48(7)	75(9)	3(7)	17(6)	-10(6)
C(21)	68(8)	52(8)	66(8)	1(6)	34(7)	-17(6)
C(22)	49(6)	56(7)	42(6)	-3(6)	17(5)	-17(6)
C(23)	76(8)	38(6)	65(8)	5(6)	45(7)	9(6)
C(24)	65(8)	50(8)	121(14)	4(9)	39(9)	-2(7)
C(25)	91(10)	44(7)	71(8)	3(7)	39(8)	10(7)

Table 6.20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for (156).

Atom	x	y	z	U(eq)
H(1A)	3533(19)	1663(17)	9574(19)	119
H(1B)	4484(19)	2219(17)	10889(19)	119
H(2)	4953(10)	4077(8)	5552(10)	44
H(3A)	5866(12)	3475(9)	4142(11)	59
H(3B)	4525(12)	2769(9)	3493(11)	59
H(6)	4232(12)	5145(10)	685(11)	61
H(7)	3205(12)	6158(10)	-1175(12)	62
H(8)	1559(12)	7385(11)	-1227(12)	62
H(9)	893(11)	7602(9)	570(10)	54
H(12)	2823(12)	8468(8)	3016(12)	54
H(13)	2320(14)	10221(11)	2956(13)	72
H(14)	202(14)	10790(10)	2954(12)	68
H(15)	-1482(14)	9568(10)	2997(13)	70
H(16)	-957(12)	7804(9)	3094(11)	55
H(18)	-357(11)	5572(9)	637(11)	57
H(19)	-2326(14)	4554(11)	89(14)	77
H(20)	-3277(13)	4095(10)	1685(13)	70
H(21)	-2273(13)	4789(10)	3796(14)	71
H(22)	-296(11)	5757(10)	4338(11)	59
H(23)	2748(13)	3685(10)	5552(12)	65
H(24A)	1066(43)	2836(91)	3958(19)	116
H(24B)	2054(41)	2568(71)	3176(64)	116
H(24C)	1548(78)	3719(25)	3208(62)	116
H(25A)	4504(65)	2464(11)	6475(48)	98
H(25B)	4096(88)	1886(36)	5098(38)	98
H(25C)	3054(30)	1890(36)	5870(85)	98

Crystallographic data (excluding structure factors) for the structures (66) and (156) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. ($C_{24}H_{24}Cl_2NOPPt$: CCDC 121672), ($C_{25}H_{26}Cl_4NOPPd$: CCDC 121673). Full data for structures (75) and (76) can be obtained as supplementary information from the American Chemical Society *via* the internet or on microfiche in some libraries (Organometallics, 1999, **15**, 2867)